Chapter 15
Ecophysiology of Plants Under Cadmium Toxicity: Photosynthetic and Physiological Responses

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Contents

Abstract Cadmium (Cd) is among the elements that exhibit a pronounced toxic effect on a variety of physiological and metabolic processes. Photosynthesis is one of the main processes of autotrophic organisms. The negative effect of cadmium on the photosynthetic apparatus leads to inhibition of many metabolic pathways that ensure the vital activity of plants. Cadmium can have a direct effect on photosystem II, decreasing the electron transfer rate and inhibiting the oxygen-generating

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complex. Besides that, under the cadmium influence, there is a violation of the structure and synthesis of pigments, a quantity reduction in open reaction center (RC), as well as inhibition of enzymes in the dark phase of photosynthesis. In addition, Cd can indirectly affect photosynthesis as a result of changes in plant water metabolism, stomata closure, and reduction in CO_2 availability for assimilation centers. Under oxidative stress caused by cadmium, the integrity of thylakoid membranes is impaired, as well as the rate of photosynthesis decreases as a result of inhibition of the activity of CO_2 fixation enzymes. At the level of the whole plant, disruption of the photosynthesis process is accompanied by a decrease in the growth rate and productivity of plants. The review discusses the toxic effects of cadmium both directly on photosynthesis and on other processes associated with it.

Keywords Cadmium · Heavy metals stress · Photosynthesis · Chlorophyll fluorescence

Abbreviations

Cd	Cadmium
Chl	Chlorophyll
C_i	Intercellular CO_2 concentration
E	Transpiration rate
ETR	Electron transport rate
F_0	Minimal level of chlorophyll fluorescence
F_m	Maximum fluorescence of dark-adapted leaves
F_v	Variable fluorescence of dark-adapted state
F_v/F_m	Potential efficiency of PSII
g_s	Stomatal conductance
OEC	Oxygen evolving complex of PSII
P_N	Net photosynthetic rate
P_N/C_i	Instantaneous carboxylation efficiency
PSII	Photosystem II
Q_A and Q_B	Bound plastoquinones of PSII
qN and NPQ	Nonphotochemical quenching
qP	Photochemical quenching
RC	Reaction center
ROS	Reactive oxygen species
Rubisco	Ribulose-1,5-bisphosphate carboxylase/oxygenase
$\varphi P_0 = TR_0/ABS$	Maximum quantum yield for primary photochemistry
Φ_{PSII}	Effective quantum yield of PSII photochemistry

15.1 Introduction

The current rapid development of industry is accompanied by an increase in the amount of toxic heavy metals in the environment, pollution of which is gradually spreading to wider areas of our planet as a result of anthropogenic activities (Silva et al. 2014). Cadmium (Cd) is ubiquitous in the soil and is distinguished by its mutagenic and carcinogenic properties (Hasan et al. 2011). Among other heavy metals, cadmium has one of the highest emission rates in the soil (Wei and Yang 2010; Zhao et al. 2010), with agricultural areas contaminated higher than urban soils (Wang et al. 2015). The use of phosphate and organic fertilizers, soil liming, sewage sludge, industrial emissions, and the mining and metallurgy industries are anthropogenic sources of Cd (Sanità di Toppi and Gabbrielli 1999; Irfan et al. 2014). Cd consumption with food is mainly due to the use of crop products (Mo et al. 2009). Cadmium can cause serious human health problems even at low concentrations (Takahashi et al. 2011). At the same time, there are no threshold values of toxic concentrations of Cd (Clemens et al. 2013).

The negative effects of heavy metals are found in all autotrophic organisms. Cadmium is a nonnutritive heavy metal that can be very phytotoxic at low concentrations (Masood et al. 2012). The content of soluble Cd is usually about 0.01–0.7 mg kg^{-1} of soil (Kovalchuk et al. 2001), but can reach 2.2–2.5 mg kg^{-1} (Samani Majd et al. 2007). Cd is easily absorbed from the soil and transferred to the aboveground organs of plants (Gallego et al. 2012), which always leads to a significant decrease in plant growth parameters (Ci et al. 2009; Li et al. 2013), causes leaf chlorosis (Liu et al. 2011), leaf rolling, and browning of root tips (Najeeb et al. 2011), which negatively affects reproduction (Xiong and Peng 2001) and induces plant senescence (Hall 2002; Maksymiec 2007) due to significant changes in many metabolic processes (Baryla et al. 2001; Singh et al. 2006)—such as photosynthesis (Wan et al. 2011), transpiration rate (*E*; Bazzaz and Govindjee 1974), chlorophyll (chl) synthesis (Jain et al. 2007), change in the chloroplast ultrastructure (Sandalio et al. 2001), stomatal conductivity (Burzyński and Żurek 2007), sugar synthesis (Moya et al. 1993), and nutrient intake (Pinto et al. 2004; Rodríguez-Serrano et al. 2009; Zhang et al. 2014)—as well as plant death (Faller et al. 2005; He et al. 2008; Hayat et al. 2014). At the molecular level, exposure to Cd can damage many vital macromolecules, such as nucleic acids, enzymes, and membrane lipids (Watanabe et al. 2003).

15.2 Cd Uptake Into the Plant

In soil, Cd^{2+} is present in soluble form and therefore is quickly absorbed by plants through the root system (Krevešan et al. 2003), which is the first place of the negative influence of these ions (Krupa and Baszynski 1995). Uptake and accumulation of Cd causes a reduction in growth and damage to the root tips (Valentovičová et al. 2010), an imbalance in the absorption of mineral nutrients and water (Gouia et al. 2000), and enzyme inactivation (Siedlecka and Krupa 1999; Soudek et al. 2014). All this causes a significant reduction in biomass, restricting the development of plants (Riaz et al. 2014), or even plant death at high Cd concentrations. At the molecular level, Cd causes irreversible changes in protein conformation due to interactions with sulfhydryl (SH) groups (Dafré et al. 1996), changes in the permeability of cell walls and membranes due to interactions with nucleophilic groups (Ramos et al. 2002), and changes in redox cell balance.

The degree of Cd absorption by the roots depends on the availability of the metal in the root formation environment (Soudek et al. 2014; Xue et al. 2018), as well as soil characteristics and temperature. Plants do not have a system for eliminating Cd from root cells, and the movement of the absorbed metal mainly occurs in a passive manner with a transpiration flow (Gallego et al. 2012). Part of uptaken Cd is adsorbed in the cell wall of the root cortex by extracellular saccharides (Bekasova et al. 2002). On the other hand, Cd can enter the plant cell using a transport system that participates in the absorption of micronutrient, for example, using transmembrane carriers of divalent metals on the plasma membrane, most likely via Ca^{2+} channels (Song et al. 2017). Absorbed Cd either enters the vacuole of the roots, or moves to the xylem for transport to aboveground organs with a transpiration flow (Sanità di Toppi and Gabbrielli 1999). The Cd accumulation in shoots linearly depends on the transpiration rate (Liu et al. 2016).

In most higher plants, there are mechanisms that prevent the movement of Cd from roots to shoots (Baker 1981). The ratio of Cd held in the roots and translocated to the leaves varies significantly among different plant species (Ekvall and Greger 2003; Tran and Popova 2013). Among the plants studied are *Noccaea caerulescens* (Lombi et al. 2002), *Sorghum bicolor* (Xue et al. 2018), *Oryza sativa* (He et al. 2008), *Brassica napus* (Larsson et al. 1998), *Dittrichia viscosa* (Fernández et al. 2013), *Lactuca sativa*, *Hordeum vulgare* (Akhter et al. 2012), *Brassica juncea* (Mohamed et al. 2012), *Cassia alata* (Silva et al. 2018), and *Carthamus tinctorius* (Moradi and Ehsanzadeh 2015), which have a specific mechanism for the Cd accumulation in the roots that reduce the transport of Cd to the shoots (Baker 1981; Pinto et al. 2004; Degl'Innocenti et al. 2014). This strategy promotes the adaptation of plants to living in soils with a high content of heavy metals (Tran and Popova 2013; Moradi and Ehsanzadeh 2015; Liu et al. 2018). A decrease in transpiration rate is often accompanied by a decrease in the influx of Cd from the roots to the shoots through the xylem and the accumulation of Cd in the roots (Fan et al. 2011). Transporting Cd is an energy-intensive process with ATP consumption produced during photosynthesis and respiration. The negative impact of Cd on these processes may indirectly contribute to the slowing down of metal translocation to aboveground organs and its accumulation in the roots (Fernández et al. 2013), although for most plants Cd is toxic even at very low concentrations in the root medium.

Total accumulation and related Cd tolerance vary greatly between different plant species, varieties, and populations (Sorić et al. 2011; Šimić et al. 2012; Franić et al. 2017). Genotypic variations in absorption and accumulation of Cd were found in

Betula pendula, *Picea abies*, *Pinus sylvestris* (Österås et al. 2000), safflower (Pourghasemian et al. 2013), *Oryza sativa* (Liu et al. 2007), and *Triticum* (Cakmak et al. 2000; Greger and Löfstedt 2004). Resistance to stress is due to the ability of the plants to accumulate various concentrations of Cd, which vary depending on the type of tissue (Wang et al. 2008). As a result of root sequestration, a limited movement of Cd is observed both in the symplast as a result of metal localization in the vacuoles and in the apoplast due to the development of apoplastic barriers (Lux et al. 2011). From the root to the stem and leaves, Cd is transported at a very weak speed (Ernst et al. 1992) that, however, significantly exceeds the translocation of other heavy metals (Burzyński and Kłobus 2004). The effect of decreasing Cd concentration in leaves can be observed as a result of increased plant growth, that is, a dilution effect (Ekvall and Greger 2003). On the other hand, redistribution of Cd to old leaves may be one of the mechanisms of stress adaptation in shoots (Maria et al. 2013). Another mechanism for increasing tolerance to Cd toxicity in leaves may be metal isolation in vacuoles (Wu et al. 2013).

Cd accumulation in the tissues of most plants gradually decreases in the direction from the roots to the leaves (Silva et al. 2018). The critical toxic concentration of Cd in the roots is higher than that in the stem and leaves, which are less tolerant to metal accumulation. Moreover, it is these tissues that are more susceptible to oxidative stress (Silva et al. 2018).

To quantify the degree of metal transfer between plant organs, several factors can be used: for example, the bioconcentration factor (BCF)—calculated as $BCF = Cd_{pt}/Cd_{ns}$, where Cd_{pt} is the Cd concentration in plant tissue and Cd_{ns} is the Cd concentration in the soil (Yoon et al. 2006)—or the translocation factor (TF), obtained as $TF = Cd_{s}/Cd_{r}$, where Cd_{s} is the Cd concentration in the shoots and Cd_{r} is the Cd concentration in roots. For example, *Cassia alata* is considered a Cd-hyperaccumulator, since is $BCF > 1$ in this plant (Silva et al. 2018). TF depends on the type and concentration of Cd in the solutions with which plants are treated (Sterckeman et al. 2011).

15.3 Plant Growth Inhibition

Excessive Cd can disrupt the vital processes of photosynthesis, respiration, and nitrogen metabolism, resulting in reduced plant growth (Sanità di Toppi and Gabbrielli 1999). A decrease in plant biomass is the best-known symptom of phytotoxicity of Cd (Feng et al. 2010; Akhter et al. 2012). Growth inhibition by even small amounts of Cd has been shown in various plant species, including *Medicago truncatula* (Saeidi et al. 2012), *Cucumis sativus* (Burzyński and Kłobus 2004), *Pinus sylvestris* (Ekvall and Greger 2003), *Juncus effuses* (Najeeb et al. 2011), *Helianthus annuus* (Laspina et al. 2005), *Vigna unguiculata* (Santos et al. 2018), *Ricinus communis*, *Brassica juncea* (Bauddh and Singh 2012), *Carthamus tinctorius* (Moradi and Ehsanzadeh 2015), barley, maize (Lysenko et al. 2015), *Brassica juncea* (Iqbal et al. 2010), tomatoes (Cherif et al. 2012), and *Atriplex* plants (Nedjimi and Daoud 2009).

The Cd effect on water and ionic plant relationships inhibits growth and photosynthesis. Cd treatment negatively affects water metabolism and is accompanied by a change in water potential, *E*, and relative water content (RWC), which correlate with the general state of plant metabolism (Flower and Ludlow 1986). Oxidation by cadmium of SH group of membrane transport proteins (Lösch 2004) leads to inhibition of the aquaporin activity (Przedpelska-Wasowicz and Wierzbicka 2011) and, as a result, impedes the water movement in plants (Irfan et al. 2014). Inhibition of H^+-ATPase activity on membranes leads to impaired absorption of nutrient ions and affects the cell division (Zhang et al. 2009; Janicka-Russak et al. 2012), which can lead to a reduction in leaf surface, premature senescence, and, as a result, cause a decrease in the total photosynthesis of plants (Krupa et al. 2002).

Cadmium toxicity adversely affects all aspects of plant growth, including root dry masses (Najeeb et al. 2011), shoot dry masses, net dry masses, plant growth, and total leaf area per plant (Li et al. 2013; Moradi and Ehsanzadeh 2015). A decrease in leaf area (Per et al. 2016) leads to a decrease in the efficiently used solar energy in the process of photosynthesis, which causes a decrease in the accumulation of dry matter in the plant. Cd stress inhibits cell division and root development in higher plants (Yi and Meng 2003). Excessive Cd caused a decrease in net dry masses and plant height, and also caused the formation of chlorotic or necrotic areas on old rice leaves (He et al. 2008). Wheat and rice showed a decrease in the length of shoots and roots, as well as net dry masses (Moya et al. 1993). A significant growth retardation and reduction in the total leaf area per plant was found in rape plants (Larsson et al. 1998) and in safflower genotypes (Moradi and Ehsanzadeh 2015). Cd treatment of rice seedlings caused a reduction in the length of the shoots and roots along with an increase in the dry masses/fresh masses ratio—an increase in this ratio due mainly to a decrease in fresh masses with almost constant dry masses (Moya et al. 1993). This indicates the effect of Cd on plant–water relations.

To explain stress-induced growth retardation, Potters et al. (2007, 2009) proposed the concept of stress-induced syndrome, according to which, during the implementation of the general acclimatization strategy, individual sublethal stresses can trigger a set of morphogenic reactions in order to reduce the negative impact of stress through directed growth processes. Apparently, part of this strategy is the intensive formation of reactive oxygen species (ROS) and an increase in antioxidant activity, as well as a change in the effects of plant hormones. Growth reduction can also occur as a result of the effects of Cd on plant development processes, namely photosynthesis and metabolite transport (Prasad and Zeeshan 2005; Burzyński and Żurek 2007), as well as cell division (Dalla Vecchia et al. 2005).

The degree of Cd toxicity for a plant depends on its content both in the soil and directly in the plant tissue. For example, according to Tian et al. (2015), with a low total content of Cd in the soil (Cd $\leq$ 5 mg kg^{-1}), the sweet sorghum phenotype does not undergo noticeable changes. However, in pea plants, growth inhibition occurred already at 5 μM Cd^{2+}, but without changing the level of chlorophyll (Wodala et al. 2012). A high total Cd content (up to 30 mg kg^{-1}) in *Sorghum bicolor* decreased plant height and dry weight (Wang et al. 2017), length and weight of roots, shoot weight, and area and number of leaves (Xue et al. 2018). However, when growing plants in nutrient solutions, a significant decrease in sorghum biomass occurred already at 10 mg Cd L^{-1} (Pinto et al. 2004), that is, Cd exposure depends on the growing medium. According to Gill et al. (2012), in garden cress, a high total Cd content in the soil (100 mg kg^{-1}) changes photosynthesis, nitrogen metabolism, and plant growth, but with a low Cd content, sulfur metabolism and antioxidant systems are activated.

A decrease in the growth of plants treated with Cd can occur as a result of impaired CO_2 fixation, which leads to a decrease in the net photosynthetic rate (P_N) (Ahammed et al. 2012), as well as due to the effects on the photosynthetic apparatus itself and membrane permeability (Fernández et al. 2013; Fan et al. 2011; Deng et al. 2014). Under these conditions, normal root growth is impaired, which limits the ability of the plant to absorb and transport nutrients. The suppression of plant growth by cadmium strongly correlates with a decrease in the chlorophyll content (Ali et al. 2015) and, as a consequence, a decrease in the rate of photosynthesis (Li et al. 2013), which can occur as a result of a violation of the pigments' ultrastructure (Feng et al. 2010).

In addition to higher plants, Cd greatly limits growth and disrupts division (Laube et al. 1980) and ultrastructure (Fernandez-Piñas et al. 1995) of microalgae cells. Numerous studies have been conducted on different species of algae (Khoshmanesh et al. 1996; Nagel et al. 1996; Mendoza-Cozalt et al. 2002; Talarico 2002; Thapar et al. 2008; Afkar et al. 2010). For example, in *Koliella antarctica*, at a high Cd concentration, an increase and deformation of cells, a change in the structure of the cytoplasm, rupture of the chloroplast membranes, and disorganization of thylakoids were observed (La Rocca et al. 2009). With a high concentration of Cd in *Koliella antarctica* (La Rocca et al. 2009), there was an increase and deformation of cells, altered structures of the cytoplasm, chloroplast sheath breaks, and disorganization of thylakoids.

In microalgae, a significant amount of accumulated Cd was associated with cell wall components (Zhou et al. 1998), which negatively affects the absorption of nutrients into cells (La Rocca et al. 2009). Cadmium may compete with other divalent cations, mainly Ca^{2+}, for the extracellular binding sites of specific membrane transporters (Zhao et al. 2002) that can lead to changes in the cellular level of Ca^{2+}, an essential element for cell growth and development.

15.4 Stomata Activity

In plants, there is an effective translocation of metal from the root to the shoot, which leads to the accumulation of Cd in the leaves. Cadmium translocation into leaves is carried out by long-distance transport, which depends on the rate of transpiration (E) and stomatal conductance (g_s). Cadmium reduces the stomatal frequency (Barceló et al. 1988), g_s (Baryla et al. 2001), and the associated CO_2 uptake (Asgher et al. 2014). This may have an indirect effect on photosynthesis by reducing the concentration of intracellular CO_2 available for assimilation, which may lead to a decrease in P_N and E (Shi and Cai 2008; Ahammed et al. 2013; Xue et al. 2018).

The decrease in g_s level in plants is due to stomata closure as a result of exposure to guard cells by Cd (Wan et al. 2011; Moradi and Ehsanzadeh 2015). Apparently, cadmium destroys the regulation of Ca^{2+} transporters, which leads to a decrease in the absorption or use of CO_2 and, ultimately, to a decrease in photosynthesis (Pietrini et al. 2010). Thus, the likely cause of Cd's influence on stomatal movement and plant–water relations associated with them could be interference of Cd in ionic movements (K^+ and Ca^{2+}) in stomatal guard cells (Poschenrieder et al. 1989; Nedjimi and Daoud 2009). Cadmium can also inhibit stomatal opening by reducing cell wall elasticity (Barceló et al. 1986). In addition, the influence of Cd on the biosynthesis of abscisic acid is not excluded.

The effect of stomatal closure, and the associated decrease in g_s, on photosynthetic ability is due to a change in intercellular CO_2 concentration (C_i) (Seemann and Critchley 1985), which leads to a restriction of CO_2 supply for assimilation into chloroplasts. The change in C_i in plants subjected to Cd stress is shown in mung bean (Wahid et al. 2008), safflower (Moradi and Ehsanzadeh 2015), and rape (Ali et al. 2015). However, it should be noted that a decrease in the efficiency of the Rubisco enzyme, by which the carboxylation process is carried out (Hasan et al. 2011), may cause C_i to increase (Barbosa et al. 2014).

There is a correlation between a decrease in instantaneous carboxylation efficiency (P_N/C_i) and an increase in C_i, which indicates inhibition of CO_2 absorption by Cd (Nwugo and Huerta 2011; Santos et al. 2018). The fall in P_N, associated with an increase in C_i, can be directly related to the influence of stressful conditions on the activity of photosynthesis. It can often be observed that a decrease in the photosynthesis rate occurs regardless of the stomata diffusion parameters, which may be due to a change in the efficiency of the photosynthetic apparatus or its size (Seemann and Critchley 1985). According to Moradi and Ehsanzadeh (2015), a decrease in P_N under the Cd influence can only be partially associated with a decrease in g_s, and reduction in photosynthesis mainly involved nondiffusion restrictions.

Stomata closure is accompanied by a decrease in E, which limits the transport of Cd from roots to shoots and minimizes the negative effects of Cd (Gratão et al. 2015). Transpiration rate reduction by Cd has been shown in honeysuckle (Jia et al. 2015), aquatic fern (Deng et al. 2014), wheat (Hayat et al. 2014), and tomato (Degl'Innocenti et al. 2014). In addition, Januškaitienė (2010) reported a decrease in water-use efficiency (WUE) of *Pisum sativum* and *Hordeum vulgare* plants subjected to Cd stress. WUE reflects the instantaneous gas exchange state of the plant (Pinzón-Torres and Schiavinato 2008) and shows the amount of fixed carbon per unit of water lost (Boutraa et al. 2010).

The effect of Cd depends on the plant species and may be associated with their anatomical features and a decrease in pigment content. For example, in *Arachis hypogaea*, Cd initiated an increase in the number of stomata and a decrease in their length in the epidermis of the leaf (Shi and Cai 2008). However, small but numerous stomata were characterized by high productivity in the CO_2 adsorption with minimal loss of water, which is typical for xerophyte plants (Sundberg 1986; Bosabalidis and Kofidis 2002). Gas exchange of plants may also depend on the anatomical features of the leaves. It is generally accepted that a large volume of palisade parenchyma corresponds to a large surface area of CO_2 absorption (Rhizopoulou and Psaras 2003). Mesophyll compartmentalization promotes less water loss, but reduces tissue conductivity for CO_2 (Terashima 1992; Miyazawa and Terashima 2001). Treatment of Cd leads to expansion of the lamina, upper epidermis, and thickness of the palisade parenchyma (Shi and Cai 2008). These anatomical features may contribute to a decrease in g_s and E and, consequently, to a P_N decrease.

The degree of toxicity of Cd in the leaves depends on its concentration. In the leaves of barley seedlings, Cd at a high concentration (80 μM and above) had a pronounced damaging effect until necrotic spots appeared, in which the metal may be excluded (Pietrini et al. 2010). However, with small concentrations or prolonged accumulation, Cd also causes a marked decrease in leaf development, but often there are no noticeable effects at the photosynthetic level, which may be due to the inclusion of efficient metal compartmentalization and/or detoxificant–repair mechanisms. Degl'Innocenti et al. (2014) also showed no effect of Cd on g_s and E, which indicates that reduction in P_N in Cd-treated plants is not associated with stomatal limitation, which was also confirmed by unchanged C_i values. In a study by Liu et al. (2018), Cd with a total content of ≤ 4 mg kg^{-1} of soil did not significantly affect the conductivity of CO_2, as a result of adaptation to the environment already at Cd ≤ 2 mg kg^{-1}.

15.5 Chloroplast Degradation

Due to a number of defense mechanisms, only very small amounts of Cd accumulate in chloroplasts (Lysenko et al. 2015). On the path of Cd movement from soil to chloroplasts is a series of barriers in the form of selective permeability of membranes and heavy metal immobilization mechanisms (Siedlecka and Krupa 1999). In leaves, cadmium can bind to polysaccharides of the cell wall or move in vacuoles. There are plants that can accumulate Cd in trichomes or isolate on the surface of leaves (Choi et al. 2001). However, a small portion of Cd remains, which penetrates into the chloroplasts.

In some microalgae, more than half of the total amount of Cd in the cell can be concentrated in chloroplasts (Nagel et al. 1996; Mendoza-Cozalt et al. 2002). However, the degree of compartmentalization of Cd strongly depends on the cells' structure in different microalgae species. For example, *Euglena* cells do not have cell walls and vacuoles and therefore approximately 60% of Cd accumulates in chloroplasts (Mendoza-Cozalt et al. 2002). The opposite situation is observed in *Audouinella saviana*, in which Cd is absent in chloroplasts, since this alga has cell walls and vacuoles (Talarico 2002).

In higher plants, the amount of Cd in chloroplasts is species-specific and depends on the time of metal accumulation. However, data on the accumulation of Cd in plant chloroplasts vary greatly among different authors, since the accumulation of

Cd in chloroplasts depended little on the concentration of metal in the soil (Lysenko et al. 2015). For example, in *Brassica napus*, chloroplasts accumulated 0.02% of leaf Cd over a long period (Baryla et al. 2001), while in *Phragmites australis*, 10–15% (Pietrini et al. 2003).

Exposure to Cd leads to degradation of the chloroplasts' structure (Horváth et al. 1996; Maksymiec 2007), mainly as a result of the destruction of thylakoid proteins and membranes (Skórzyńska-Polit and Baszyński 1997). In addition, chlorophyll degradation can occur enzymatically due to Cd-inducible chlorophyllase (Hasan et al. 2011). The presence of Cd reduces the number of chloroplasts when calculated per cell and unit leaf area (Fagioni et al. 2009). However, there are observations when the net CO_2 assimilation ratio per unit leaf area decreases, but does not change per unit chlorophyll (Pietrini et al. 2003).

Li et al. (2016) observed a Cd-induced reduction of Ca^{2+} content in the roots, stems, and leaves of *Allium fistulosum*. A decrease in the concentration of Ca^{2+} after exposure to Cd causes damage to intracellular binding proteins, which leads to disruption of membranes integrity (Lu et al. 2010). In barley plants, Cd treatment reduced the K^+ content in both the thylakoids and stroma of the chloroplast, as well as the Mn^{2+} concentration in thylakoids. In addition, in the presence of Cd, there is a decrease in the content of Cu^{2+} in thylakoids and Ca^{2+} in the stroma, but an increase in Ca^{2+} and Fe in thylakoids and Mg^{2+} in the stroma is simultaneously observed (Lysenko et al. 2019). After Cd treatment, a decrease in Mg^{2+} was also observed in leaves, stems, and roots (Liu et al. 2015). In the roots and leaves, some researchers found a decrease also in the Fe and Mn content (Basa et al. 2014; Ali et al. 2015). Cadmium stress greatly reduces the Cu^{2+} and Zn^{2+} content in chloroplasts (Tang et al. 2013; Santos et al. 2018). The absorption of Zn^{2+} in chloroplasts may reduce due to the competition of Zn^{2+} with Cd^{2+} for space in the carrier, while the treatment of Cd does not reduce the total content of Zn^{2+} in the leaves (Gallego et al. 2012).

Lysenko et al. (2019) showed that after Cd treatment, the amount of Ca^{2+} in the stroma decreased when calculating per mg of Chl in the whole chloroplast, but increased in thylakoids, while the content of Mg^{2+} in the stroma increased with a constant content in thylakoids. Since, compared with Mg^{2+} and Ca^{2+}, the accumulation of Cd^{2+} was insignificant, competition between these metals was unlikely. This process may be a plant defense mechanism against the penetration of Cd^{2+} into the thylakoids, and Ca^{2+} may be an effective competitive inhibitor of the action of Cd^{2+} on the oxygen evolving complex (OEC; Faller et al. 2005), while Mg^{2+} does not appear to be involved in these events (Sigfridsson et al. 2004). Most likely, part of Ca^{2+} is transported from the stroma to thylakoids, while Mg^{2+} is sent to the stroma. This may serve as a mechanism for protecting thylakoids from exposure to Cd^{2+}. Moreover, the total concentration of divalent cations in chloroplasts does not change.

Under the influence of high Cd concentrations, chlorophyll (Chl) is degraded in plant leaves (Pietrini et al. 2003; Shi and Cai 2008; Wan et al. 2011; Silva et al. 2012; Liu et al. 2018; Xue et al. 2018), although a decrease in the carotenoid (Car) content was also noted (He et al. 2008; Shi and Cai 2008; Moradi and Ehsanzadeh 2015). A decrease in Chl content can partially explain the decrease in P_N observed with Cd stress (Xue et al. 2018). Cd can interfere with Chl synthesis (Burzyński and

Kłobus 2004; Laspina et al. 2005; Nedjimi and Daoud 2009; Moradi and Ehsanzadeh 2015) by inhibiting Δ-aminolevulinic acid dehydratase (EC 4.2.1.24) and protochlorophyllide reductase (EC 1.3.1.33; Ci et al. 2010), due to the interaction of Cd with sulfhydryl groups (Prasad and StrzaŁka 1999). The effect of Cd on the Chl content can also be carried out indirectly due to a nutritional deficiency (Van Assche and Clijsters 1990). Cadmium inhibits Fe uptake by roots, which can lead to leaf chlorosis (Siedlecka and Krupa 1999). Analogous results were obtained in the *Brassica juncea* leaves (Ebbs and Uchil 2008), although Pietrini et al. (2003) exclude the chlorophyll loss possibility due to low levels of Fe in the leaves. Chl and Car levels may also fall as a result of oxidative stress caused by Cd (Cherif et al. 2012).

Cd ions have a constant valence, and therefore its effect on the redox balance of the cell can be carried out indirectly, apparently by substituting divalent metals in enzymes (Maret and Moulis 2013). Cd^{2+} can replace Mg^{2+} in tetrapyrrole centers of Chl, which causes molecular degradation of the light-harvesting complex II (LHCII) (Gillet et al. 2006; Wang et al. 2014). Perhaps this process is one of the main mechanisms of the negative effect of Cd on plant photosynthesis (Küpper et al. 1998). However, the Cd^{2+}/Chl ratio in plant chloroplasts under natural conditions is very low (1/1000) (Lysenko et al. 2015). The maximum Cd^{2+}/Chl ratio reaches 1/257 (Geiken et al. 1998). However, according to Lysenko et al. (2015), Cd^{2+} affects only a very insignificant part of Chl antennas, and therefore the widespread opinion about the significant effect of ion substitution in Chl on plant photosynthetic productivity should be considered insolvent.

Many studies have reported that as Cd-induced leaf chlorosis develops, the ratio Chl *a*/*b* increases (Shi et al. 2003), although Shi and Cai (2008) in *Arachis hypogaea* observed only synchronous mixing of both Chl types. The value of Chl *a*/*b* can increase as a result of an increase in the content of Chl *a*, as well as a decrease in the content of Chl *b*. In addition, leaf chlorosis can be caused by both direct and indirect effects of Cd on the content of both types of Chl (Ebbs and Uchil 2008).

Chl *b* pool was shown to have a greater effect on chlorosis than Chl *a* pool (Angadi and Mathad 1998; Fargaová 2001). A change in the ratio of the two forms of Chl can be associated either with a decrease in the transition of Chl *a* to Chl *b*, or with an increase in the reverse reaction of Chl *b* in Chl *a*. In higher plants, the predominant form is Chl *a*. Auxiliary pigment Chl *b* is formed in a reaction with Chl oxygenase, as a result of which the methyl group of the porphyrin ring transfers to the formyl group (Porra et al. 1994). This enzyme is light-dependent and was found not only in higher plants, but also in microalgae (Masuda et al. 2003).

According to Ebbs and Uchil (2008), the preferred loss of Chl *b* during Cd stress is most likely to result from the conversion of Chl *b* into Chl *a*. A similar conversion of pigments was found in a number of plants (Ito and Tanaka 1996) and is carried out using ferredoxin-dependent Chl *b* reductase through the formation of hydroxymethyl, as occurs with the formation of Chl *b* (Scheumann et al. 1998). Similar Chl transformations can be part of the adaptive mechanism of plants under conditions of changing light intensity. Chlorophyll *b* is released from the PSII conglomerates and then transformed to form the reaction center (RC) of the Chl *a* molecule (Ohtsuka et al. 1997).

Transformation of Chl *b* into Chl *a* also occurs during catabolic processes during aging (Scheumann et al. 1998), involving enzymes that decompose Chl *a* but not Chl *b* (Dangl et al. 2000). The formation of ROS induced by Cd or nutritional deficiency (K, Mg, Zn) can also cause leaf aging with a corresponding loss of Chl *b* (Marschner 1995). For example, in *Brassica napus*, catalase gene expression increased during aging, and in *Zea mays*, expression of glutathione-S-transferase (GST; EC 2.5.1.18) increased (Dangl et al. 2000). Cd also increased expression of these two enzymes (Lang et al. 2005). An increase in Chl *a*/*b* may be due to the initiation of catalase activity during Cd stress, as shown in *Brassica juncea* (Singh and Tewari 2003). According to Ebbs and Uchil (2008), the predominant decrease in Chl *b*, aging, and Cd-induced chlorosis are associated with similar processes under oxidative stress, namely, an increase in the transformation of Chl *b* into Chl *a* and a simultaneous decrease in Chl oxygenase activity. The active reduction of Chl *b* in Chl *a* probably serves to compensate for the Cd-induced decrease in Chl synthesis and prevents the destruction of photosynthetic machinery.

15.6 Photosynthesis

The photosynthetic apparatus is one of the main objects of Cd action in phototrophic organisms (Prasad and StrzaŁka 1999; Ci et al. 2010; Cherif et al. 2012). The inhibitory effect of Cd on P_N is shown in various plant species (Krupa and Baszynski 1995; Di Cagno et al. 1999; Silva et al. 2018), including maize (Wang et al. 2009; Lysenko et al. 2015; Silva et al. 2017), legumes (Vassilev et al. 2005), rice (Moya et al. 1993; Wang et al. 2014; He et al. 2008), soybeans (Xue et al. 2013), sweet sorghum (Xue et al. 2018), *Brassica campestris*, *Brassica juncea* (Chen et al. 2011), and *Ceratopteris pteridoides* (Deng et al. 2014). Moreover, the degree of negative influence of Cd depends on the type of plant photosynthesis (C3 or C4). C3 plants are more tolerant of high Cd concentrations (Inouhe et al. 1994) and suffer less from leaf chlorosis (Siedlecka and Krupa 1999).

Cd causes negative changes at both the structural and functional levels of the organization of the photosynthetic apparatus of plants (Singh et al. 2006; Cherif et al. 2012). Under Cd stress, there may be a deterioration in chlorophyll synthesis (He et al. 2008), damage to thylakoid membranes (Maksymiec 2007), impaired electron transport (Pagliano et al. 2006), and inhibition of the effectiveness of PSII and CO_2 assimilation enzymes, and Rubisco and phosphoenolpyruvate carboxylase (PEPC; Burzyński and Kłobus 2004; Tran and Popova 2013; Masood et al. 2012; Li et al. 2015). The photosynthetic rate can also be reduced by inhibiting ferredoxin-NADP$^+$ reductase (EC 1.18.1.2; Costa et al. 2012) and ATP synthase when Cd interacts with the functional sulfhydryl groups of these enzymes (Van Assche and Clijsters 1990). Cd has been shown to negatively affect the state of PSII protein complexes (Ahmed and Tajmir-Riahi 1993).

15.6.1 Light Phase of Photosynthesis

The multiple effects of Cd toxicity can be the cause of inhibition of the photosynthetic electron transport. High Cd concentrations very quickly reduce the functional activity of photosystem II (PSII; Baszyński 1986; Burzyński and Kłobus 2004; Wodala et al. 2012; Moradi and Ehsanzadeh 2015), but not photosystem I (PSI; Bazzaz and Govindjee 1974; Küpper et al. 2007). PSII photosynthetic electron transport is already inhibited at low Cd^{2+} concentrations (5 μM), as evidenced by a decline in the effective quantum yield of PSII photochemistry (Φ_{PSII}), the maximum electron transport capacity (ETR_{max}), and the maximum quantum yield for electron transport.

It is assumed that the target sites of Cd action are located on both sides of the PSII, donor and acceptor (Pagliano et al. 2006). On the donor side, Cd^{2+} can exchange with the Ca^{2+} ions of the Ca/Mn cluster in the oxygen evolving complex (OEC) (Faller et al. 2005). Šeršeň and Kráľová (2001) observed a direct effect of Cd^{2+} on the Mn ion cluster located in the OEC. In this case, Cd caused the release of Mn^{2+}, which inactivated the electron transport from H_2O to the reaction center of photosystem II. This hypothesis is also supported by the fact that a decrease in the Mn^{2+} content was found in the thylakoids, but not in the chloroplast stroma in the Cd-stressed plants (Lysenko et al. 2019). Thus, the damaging effect of heavy metals consists in displacing Mn^{2+}, Ca^{2+}, and Cl^-, important cofactors necessary for water-splitting systems (Krupa and Baszynski 1995; Faller et al. 2005). On the other hand, under the action of Cd, a change in the OEC polypeptide composition can occur (Skórzyńska and Baszyński 1993).

On the acceptor side of PSII, Cd^{2+} most likely binds to Q_B and not to Q_A (Sigfridsson et al. 2004). According to Parmar et al. (2013), Cd is able to act on nonheme Fe in the Q_A-Fe-Q_B complex and cause a molecular reorganization of Q_B, thereby reducing the electron transport rate (ETR). On the other hand, according to Paddock et al. (2003), conformational modification of Q_B may also occur due to protonation of histidine residues. In addition, Ishikita and Knapp (2005) showed that inhibition of electron transport can occur due to the interaction of Cd with tyrosine residues in protein D1–161. In any case, inhibition of the electron transfer rate can lead to inhibition of OEC (Bazzaz and Govindjee 1974; Tripathi et al. 1981).

Inhibition of photochemical processes may also be due to inhibition of the Calvin cycle under Cd stress. In this case, there is a decrease in the consumption of ATP and NADPH, which is accompanied by a violation of the ΔpH on thylakoid membranes (Krupa et al. 1993). As a result of this, the electron transfer and quantum efficiency of PSII are reduced (Zribi et al. 2009). Exposure to Cd causes stomata to close, which leads to CO_2 limitation, the accumulation of ATP and NADPH, and, as a result, to the disturbance of photosynthetic machinery (Sayed 2003).

The degree of damage to PSII by Cd is strongly due to light conditions (Küpper et al. 2002). With minimal illumination, the suppression of PSII by Cd is mainly due to the disruption of the light-harvesting antenna functions, since Mg^{2+} in Chl II molecules is replaced by Cd^{2+}. At maximum illumination, the destruction of the PSII reaction center may be observed (Küpper et al. 2002).

Photosystem I is considered to be relatively insensitive to the action of Cd^{2+} (Pál et al. 2006). However, in the case of Cd-induced Fe deficiency in plants, some researchers observed inhibition of electron fluxes around PSI (Siedlecka and Baszynski 1993; Šeršeň and Kráľová 2001; Timperio et al. 2007). Wodala et al. (2012) also reported a reduction in the Φ_{PSI} and the number of electrons in the intersystem chain under Cd stress. Cd acts on PSI mono- and multimeric complexes, disrupting the stable binding of Chl to lipoproteins and, therefore, reducing the number of PSI complexes (Sárvári 2005; Fagioni et al. 2009). In addition, Cd can cause a decrease in the flow of electrons to the PSI from stromal donors. The potential sources of electrons from the stroma can be peripheral ferredoxin and pyridine nucleotides, primarily NADH and NADPH, which can also serve as carriers of electrons from the triozo phosphate pool in the stroma (Asada et al. 1992). Chow and Hope (2004) suggest that electrons from pyridine nucleotides can then be directed to the plastoquinone pool using NAD(P)H dehydrogenase. Ascorbate may also act as an additional potential source of electrons.

15.6.1.1 Chlorophyll Fluorescence

Under the influence of environmental changes, there is a correction of the working capacity of photosynthetic machinery. Under stressful conditions, plants require less light energy for photosynthesis. Overabundant photon energy is gently scattered in the form of heat by chlorophyll fluorescence to prevent photoinhibition and photooxidation. Changing the parameters of the fast-polyphase fluorescence of the induction transient process allows us to register a violation of the functional state of photosynthesis under stress (Strasser et al. 2004). Moreover, there is a close correlation between Chl fluorescence and the physiological state of the photosynthetic apparatus. Changes in Chl fluorescence parameters reflect the intensity of heavy metal stress (Baker and Rosenquist 2004; Żurek et al. 2014), including Cd stress (Sheoran et al. 1990; Larsson et al. 1998; Di Cagno et al. 1999; Krupa and Moniak 1998; Burzyński and Żurek 2007). Measurement of Chl fluorescence parameters allows obtaining information on the functional state of photosystems. The most important among these parameters are the F_0 (minimal level of chlorophyll fluorescence), F_{m} (maximum fluorescence of dark-adapted leaves), F_{v} ($F_{\mathrm{v}} = F_{\mathrm{m}} - F_0$; variable fluorescence of the dark-adapted state), $F_{\mathrm{v}}/F_{\mathrm{m}}$ (potential efficiency of PSII), and fluorescence curves reflecting phenomenological energy flows (Kalaji and Łoboda 2007; Tuba et al. 2010).

The negative effect of Cd is observed at different stages of the photosynthesis light phase (Maksymiec and Baszyński 1996). The effect of Cd on the electron transport rate in photosystems is determined by measuring fluorescence parameters such as $F_{\mathrm{v}}/F_{\mathrm{m}}$ and Φ_{PSII}, and qP (photochemical) and qN, NPQ (nonphotochemical quenching of the excited state of chlorophylls) (Liu et al. 2011; Ahammed et al. 2012). A decrease in these parameters with Cd stress is shown in many plant species (Filek et al. 2010; Pietrini et al. 2010), as well as in some types of hyperaccumulators (Küpper et al. 2007). However, the degree of influence of Cd is individual in each plant species and varieties, which can be explained by the different values of Cd penetration into chloroplasts. For example, prolonged exposure to Cd reduced the F_v/F_m and Φ_{PSI} in some varieties of barley and did not affect these parameters in other varieties (Wu et al. 2003). At a high Cd content (up to 600 μM) in maize seedlings, the PSII photochemical activity (F_v/F_m, Φ_{PSII}, qP, ETR) decreases only in a sensitive, but not in a tolerant line (Ekmekçi et al. 2008).

The minimum chlorophyll fluorescence (F_0) level increases under stress due to a decrease in the efficiency of electron transfer from the Chl *a* antenna to the RC of PSII or when these centers are damaged (Ralph and Burchett 1998; Pietrini et al. 2003). A decrease in F_0 can occur if inactive PSII centers function as scattering sinks (Larsson et al. 1998). Shi and Cai (2008) in peanut plants already at 10 μM Cd showed a sharp increase in F_0 as a result of a decrease in F_v/F_m and F_v/F_0. It is also interesting to note that the *Tradescantia* plants showed an increase in F_0 at 3 h, but a decrease in F_0 at 5 h Cd exposure (Judy et al. 1990).

With an increase in the Cd content, F_m also decreases (Franić et al. 2017), apparently, as a result of violation of the thylakoid membrane ultrastructure (Ekmekçi et al. 2008). This reduces the time to reach F_m (t_{max}), which indicates the stress state of the plant. Because F_m reflects PSII functionality when all Q_A are reduced, shortening t_{max} implies a decrease in the Q_A pool suitable for reduction (Mallick and Mohn 2003). After Cd treatment, the value of V_J (variable fluorescence at J step) increases, which implies a decrease in the effectiveness of Q_A^- reoxidation (accumulation of reduced Q_A^-), since V_J determines the value of part of the reduced Q_A^- (Kalaji et al. 2014). S_m indicates how many electrons move in the electron transfer chain (Stirbet and Govindjee 2011). A decrease in S_m under stress indicates that F_m can be achieved faster, because fewer electrons are used to reduce PSII acceptors. This is also observed when the parameter t_{max} decreases. Under stressful conditions, the primary incline of the relative fluorescence (M_o) increases, corresponding to the relative rate of Q_A reduction (Christen et al. 2007).

When exposed to Cd, a decrease in F_v/F_m is observed, which indicates a slowdown in electron transport in PSII (Pietrini et al. 2003; Sigfridsson et al. 2004; Küpper et al. 2007; Ahammed et al. 2013; Parmar et al. 2013; Moradi and Ehsanzadeh 2015; Liu et al. 2018) and is always used as a stress indicator (Linger et al. 2005). Shi and Cai (2008) observed a decrease in F_v/F_m and F_v/F_0 with a simultaneous change in Chl/Car, which indicates a change in the location of chlorophylls in thylakoids, leading to a decrease in photochemical potential (Gruszecki et al. 1991).

Basa et al. (2014) in *Beta vulgaris* found that Φ_{PSII} significantly decreases with Cd toxicity, which corresponds to a decrease in electron transfer in PSII apparently due to the destruction of RC (Váňová et al. 2009). A decrease in Φ_{PSII} under Cd stress may be the result of an increase in qN, which is an indicator of the dispersion of light as heat in plants (Per et al. 2016). Under Cd stress, an imbalance arises between the total amount of absorbed light and the number of photons used to generate energy in chloroplasts. Excessive light energy provokes the appearance of stable triplet forms of Chl, causing oxidative destruction of membranes (Sárvári 2005).

According to Janeczko et al. (2005), Cd reduced specific energy fluxes calculated per cross section of the sample (CS). Herewith, a slowdown in photosynthetic electron transfer was observed due to a decrease in the number of active reaction centers (RCs) of PSII capable of Q_A reduction. At the same time, Cd increased the amount of excitation energy that is dissipated as heat (DI_0/CS). This was accompanied by a decrease in the maximum quantum yield for primary photochemistry (φP_0) and efficiency, while the trapped exciton was able to travel the electron to the electron transport chain to a greater extent than Q_A^- (Ψ_0). Due to Cd-induced significant damage at some RC of PSII and a slight decrease in photon absorption by the antenna system (ABS) per CS, there is increased absorption flux per RC (ABS/RC), trapped energy flux per RC (TR_0/RC), and dissipated energy flux per RC (DI_0/RC).

At low Cd concentrations, it can often be observed that this heavy metal does not affect the photosynthetic electron transport (Wu et al. 2003; Burzyński and Żurek 2007; Tang et al. 2013). For example, in cotyledons and leaves of cucumber at 20 μM Cd (Burzyński and Żurek 2007), despite a sharp inhibition of P_N and g_s, the potential efficiency of PSII remained unchanged, and the only diminished fluorescence parameter was Φ_{PSII}. This can be explained by a decrease in the activity of carbon metabolism or insufficient use of ATP and NADP during CO_2 assimilation (Subrahmanyam and Rathore 2000). Di Cagno et al. (1999) also found changes in Φ_{PSII}, qP, and quantum efficiency of active RC of PSII (Φ_{exc}) with unchanged F_v/F_m in sunflower plants (10 or 20 μM Cd). The F_v/F_m ratio did not change in tomato leaves treated with Cd (Degl'Innocenti et al. 2014). However, other authors obtained opposite results in hyperaccumulator plants (Mobin and Khan 2007). The potential effectiveness of PSII remains unchanged if the F_v/F_m ratio exceeds 0.8 (Björkman and Demmig 1987). Degl'Innocenti et al. (2014) suggested that the short-term effect of Cd on tomato plants only moderately affects the reoxidation rate of the primary PSII acceptor. This effect caused only a slight shift in the ETR and Φ_{PSII} values due to a decrease in CO_2 assimilation. In contrast to the studies of a number of authors (Krupa et al. 1993; Castagna et al. 2013), Degl'Innocenti et al. (2014) showed that the content of Chl did not change in plants treated with Cd, which indicates the absence of inhibition of Chl biosynthesis and oxidation. At the same time, the presence of Cd inhibited plant growth without significantly affecting photosynthesis. It is possible that a decrease in growth and P_N without changes in Chl fluorescence parameters may be observed if plants partially adapted to Cd stress, as was shown in tomatoes (Degl'Innocenti et al. 2014).

After processing Cd of barley and corn seedlings, there were no essential changes in the values of such fluorescence parameters as F_v/F_m, Φ_{PSII}, and qP (Lysenko et al. 2015). The two nonphotochemical coefficients, qN and NPQ, changed independently, because, although both coefficients operate with F_m and F'_m (maximum fluorescence of light-adapted leaves), qN operates with F'_0 (fluorescence in leaves previously exposed to light) and NPQ does not. The literature describes cases where qN and NPQ have varied in different directions (Lichtenthaler et al. 2005).

The nonphotochemical quenching ratio of the Chl excited state (NPQ) tends to increase after Cd treatment (Pietrini et al. 2010). However, Liu et al. (2010) showed a decrease in NPQ under the action of Cd, associated with the fast-relaxing component of NPQ (qE), which determines the excitation of thylakoid membranes. At the same time, the slow-relaxing component of NPQ, depending mainly on photoinhibition (qI), changed insignificantly. This coefficient depends on the photoinhibition of PSII and on the dislocation of the light-harvesting complex outside the PSII. An increase in qI may be associated with an increase in the concentration of Cd in chloroplasts, while a decrease in qE depends on the external concentration of Cd and is species-specific. For example, in corn chloroplasts, NPQ remained almost unchanged, while in barley chloroplasts it decreased significantly (Lysenko et al. 2015).

According to Lysenko et al. (2015), in chloroplasts, Cd has two effects. The first effect, responsible for the decrease in ΔpH of membranes, reduces NPQ and is more responsive to the presence of Cd in the soil. The second effect causes photoinhibition or transformation of PSII antennas, increases nonphotochemical quenching, and is more responsive to the presence of Cd inside chloroplasts. In case of equal values of these changes, the final effect cannot be seen. For example, at 80–200 μM Cd, qI increases, qE decreases, and the net NPQ remains unchanged (Lysenko et al. 2015). Similarly, in pea leaves at 50 μM Cd, the second effect took precedence and qN rose, at 1 mM Cd the effects were the same and qN remained unchanged, and at 5 mM Cd the first effect dominated and qN decreased (Geiken et al. 1998).

The degree of negative influence of Cd on photosynthetic light reactions depends on the stage of leaf growth. Thus, in young leaves of *Phragmites australis*, the F_v/F_m ratio was high even at high Cd concentrations, since F_m decreased proportionally to F_0, which probably indicates poised damage or effective adaptation of the photosynthetic machinery under stressful conditions (Pietrini et al. 2003). However, in fully mature leaves, F_v/F_m was greatly reduced, with leaf chlorosis and destructive consequences for PSII. *Phragmites australis* appears to have a specific ability to protect plastids from the negative effects of Cd, and this ability has been found to be high in young leaves, but not in old leaves (Fediuc and Erdei 2002). Similar results were also obtained in different parts of the same rye leaf (Krupa and Moniak 1998).

When studying transient processes of fluorescence induction for 1 s, the key states are F_0 and F_m (Strasser et al. 2004). The intermediate points between these extremes, named K (300 μs), J (2 ms), and I (30 ms), determine the electron flux between the various components of the PSII. The state of these components is described by an informative O-J-I-P curve (Boisvert et al. 2006).

When disposing off absorbed photons in RC of PSII, some energy is needed to initiate electron transfer from Q_A to PSI. The apparent activation energy (AAE), associated with the rapid increase in fluorescence Chl *a*, is of great importance for studying the bioenergetics of various stages of electron transfer in PSII. The study of apparent activation energies in thylakoid membranes is carried out in order to analyze the transient processes of O-J-I-P fluorescence, in order to study the various stages of recovery of Q_A, Q_B, and PQ. Depending on the degree of oxidation–reduction of the pools Q_A, Q_B, and PQ, the apparent activation energies of PSII differ in the primary source (Boisvert et al. 2006). The rapid increase in Chl *a* fluorescence is used to study acceptor systems other than PSII, namely, the OEC and PSI (Schansker et al. 2005). Depending on the site of exposure, Cd may have different effects on electron transfer and cause a change in the apparent activation energies of PSII.

In chloroplasts, Cd can bind to chlorophyll–protein complexes and causes an imbalance between photon absorption and electron transport in PS (Bashir et al. 2015). To detect PSII damage, transient analysis is used according to the JIP test. In *Sorghum bicolor*, Cd induced an increase in DI_0/RC, ABS/RC, TR_0/RC, and ET_0/RC (electron transport flux per RC), and a significant decrease in φP_0, Ψ_{Eo} (probability that an electron moves further than Q_A^-), δ_{Ro} (probability that an electron is transported from the reduced intersystem electron acceptors to the final electron acceptors of PSI), PI_{abs} (performance index), and RC/CS_0 (Q_A-reducing RC per CS) (Xue et al. 2018). The decrease in Ψ_{Eo} and δ_{Ro} showed that the PSII electronic transfer was blocked due to the accumulation of Q_A^-. An increase in DI_0/RC, ABS/RC, TR_0/RC, and ET_0/RC, and a decrease in RC/CS_0 means inactivation of part of the active RC, possibly due to a decrease in the Chl concentration and also a decrease in the Chl *a*/*b* ratio when processing Cd (He et al. 2008). The functional significance of such fluorescence parameters as ABS/RC, φP_0, and Ψ_{Eo} can be combined using the performance index (PI_{abs}), the value of which is closely related to the possibility of energy conservation in photosystems and their activity. A marked reduction in PI_{abs} with an increase in Cd content in Sorghum bicolor leaves indicates a slowdown in electron transport and inhibition of photosynthesis (Xue et al. 2018).

According to Franić et al. (2017), in corn leaves, the toxic effects of Cd are manifested in a reduction in quantum yield of PSII electron transfer and in the efficiency of excitation energy capture by active RC of PSII (TR_0/ABS, ET_0/ABS, and ET_0/TR_0). The reduction in acceptor side-dependent yields (ET_0/ABS, ET_0/TR_0), which denote the efficiency of electron transfer, suggests the stimulation of photoinhibition in response to Cd action (Pagliano et al. 2006).

Cd treatment results in a decrease in TR_0/ABS (= φP_0), which is associated with the photoinhibition process (Turnau et al. 2008). An increase in ABS/RC with Cd treatment (Janeczko et al. 2005; Franić et al. 2017) indicates that part of the open RCs were closed or expanded the antenna size (Krüger et al. 1997). Simultaneously with a change in these parameters decreases the density of the RC per excited CS (RC/CS_0) and the density of the RC on Chl *a* basis (RC/ABS). Inactivation of the RC can be a downregulation protective mechanism against photoinhibition. The increase in TR_0/RC observed with Cd treatment (Franić et al. 2017) may indicate damage to the OEC (Kalaji et al. 2014). Exposure to Cd significantly increases energy dissipation (DI_0/RC), which is associated with leaf protection from oxidative stress, that is, absorbed excess light energy is dissipated instead of being used in Q_A^- reduction (Franić et al. 2017). PI_{ABS}, which is defined as the ability for the accumulation of exciton energy to restore intersystem electron acceptors, is rated as $(RC/ABS)(TR_0/ABS - TR_0)(ET_0/TR_0 - ET_0)$. An increase in PI_{ABS} with Cd processing occurs due to an increase in all three parameters, but the component $ET_0/(TR_0 - ET_0)$ has the most influence (Franić et al. 2017), which implies an increase in CO_2 assimilation, since a link was established between electron transfer in the photosystem and the CO_2 absorption (Krall and Edwards 1992). However, an increase in electron transfer can also be associated with other processes in the cell

(Kalaji et al. 2016). An increased PI_{ABS} value means an improvement in the overall efficiency of the photosynthetic apparatus. Some corn hybrids showed a decrease in PI_{ABS} when processing Cd, which may be due to a decline in all components of PI_{ABS}, but especially RC/ABS values (Franić et al. 2017), indicating that most of the reaction centers were inactivated (Żurek et al. 2014; Begović et al. 2016).

In some cases, after Cd treatment, an increase in Chl *a* content is observed (Aghaz and Bandehagh 2013; Franić et al. 2017), which is accompanied by a rise in F_0, F_{150}, and F_{300}. Under these conditions, stress is apparently associated with functional damage to the photosynthetic apparatus, which was accompanied by a rise in energy leakage per RC and by the reduction of TR_0/DI_0 (Strasser et al. 2000). An increased content of Chl can also be observed when plants adapt to the presence of Cd or at its low content (Chaneva et al. 2010).

15.6.2 Dark Phase of Photosynthesis

It has been shown that, in isolated chloroplasts, CO_2 assimilation slows down during Cd treatment, but no change in photochemical reactions occurs, that is, P_N deceleration by Cd occurs at the level of dark photosynthesis reactions. Weigel (1985) suggested that inhibition of Cd occurred either at the level of CO_2 fixation or as a result of a change in the activity of the Calvin cycle enzymes. Impairment of the activity of ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco, EC 4.1.39) and other enzymes of the dark stage of photosynthesis upon exposure to Cd was recorded in various plants (Prasad and StrzaŁka 1999; Burzyński and Żurek 2007; Mobin and Khan 2007).

The negative effects of Cd^{2+} observed in the carboxylation phase of photosynthesis (Weigel 1985; Di Cagno et al. 1999) can lead to inactivation of enzymes through reactions with their thiol groups (Fuhrer 1982). The main target of Cd exposure is two key enzymes of photosynthetic fixation of CO_2, Rubisco and phosphoenolpyruvate carboxylase (PEPC; EC 4.1.1.31) (Krantev et al. 2008). Cd^{2+} is able to reduce Rubisco activity by replacing Mg^{2+} in the catalytic center of the enzyme, which fixes CO_2 (Siedlecka et al. 1998). High concentrations of Cd^{2+} also lead to irrecoverable dissociation of Rubisco subunits (Lhcb1 and Lhcb2), resulting in complete enzyme inhibition (Malik et al. 1992; Hajduch et al. 2001).

It is often observed that a reduction in the maximum Rubisco activity during Cd stress is accompanied by only a slight decrease in the Rubisco protein content (Pietrini et al. 2003). A decrease in Rubisco activity may be due to Cd-induced oxidative stress or due to action of proteases activated by ROS (Prasad 1996; Romero-Puertas et al. 2002). ROSs can directly influence the dissociation of Rubisco subunits (Ishida et al. 1999). It is also possible that the decrease in Rubisco activity is associated with inhibition of Rubisco activase (EC 4.1.1.36), which has the large Cys thiol residues subunit (Portis 2003) in the carboxy terminus, with which Cd binds.

There is evidence of the effect of Cd on Calvin cycle enzymes in the stroma of chloroplasts (Prasad and StrzaŁka 1999). The phosphoglycerate kinase (EC 2.7.2.3) and glyceraldehyde-3-phosphate dehydrogenase (EC 1.2.1.12) enzymes, which are necessary during the recovery phase of the Calvin cycle, are inhibited to some extent by Cd (Sheoran et al. 1990). In addition, Cd reduces the potential activity of phosphoglycerate kinase, which indicates the effect on the synthesis of this enzyme. Decline of CO_2 reduction may affect photochemical efficiency. A decrease in Φ_{PSII} can occur as a result of a disequilibrium between the absorbed light energy and that part of it that is used in the carboxylation reaction (Burzyński and Kłobus 2004).

Cd negatively affects the dark and light stages of photosynthesis, but the site of the primary effect of Cd on photosynthesis depends on the specific conditions of the experiment, and the concentration and duration of Cd processing. For example, in maize seedlings, the degree of P_N decrease and the time of manifestation of the plant response to Cd treatment depended on the metal concentration (Wang et al. 2009). Prolonged Cd processing can cause significant metabolic changes, reflecting various interrelated processes in plants. According to Burzyński and Kłobus (2004), the effect of Cd on photosynthesis reactions is rather indirect, for example, due to changing numerous physiological processes. Cd reduces the rate of Fe transport into leaves, and low Fe content interferes with Chl synthesis and changes the chloroplasts' ultrastructure, which affects both stages of photosynthesis (Siedlecka and Krupa 1999). Cd also reduces the amount of OEC (Janeczko et al. 2005); disrupts water metabolism (Poschenrieder and Barceló 1999), assimilation, and distribution of nutrients (Krupa et al. 2002); induces oxidative stress (Dietz et al. 1999); and, as a result, inhibits leaf growth and reduces the total area for light absorption.

Burzyński and Kłobus (2004) noted that among other parameters of photosynthesis, Cd had the most noticeable effect on P_N, which suggests that Rubisco and Calvin cycle enzymes are more susceptible to Cd than light photosynthesis reactions. At the same time, a sharp decrease in P_N was apparently not associated with the influence of Cd on stomata activity, since, despite the low value of g_s, the values of C_i remained at a sufficiently high level. P_N independence from g_s has been proposed by Sheoran et al. (1990). Increased C_i values are probably associated with a decrease in P_N or with activation of dark respiratory processes stimulated by exposure to Cd (Romanowska et al. 2002) and usually associated with leaf aging. However, Shi and Cai (2008) showed that in *Arachis hypogaea*, Cd-induced P_N inhibition is mainly associated with changes in Chl and g_s, and an increase in C_i indicates inhibition of dark photosynthesis (Sas et al. 2006).

The toxicity of Cd^{2+} is manifested at varying degrees depending on the stage of plant development. So, at the early stage of vegetation of the plant pigeonpea (*Cajanus cajan* L.), 0.5 and 1.0 mM Cd^{2+} resulted in a 50% reduction in photosynthesis and activity of photosynthetic carbon reduction polymerase chain reaction (PCR)-cycle enzymes (Rubisco, phosphoglycerate kinase, NAD(P)-glyceraldehyde-3-phosphate dehydrogenase, and aldolase (EC 4.1.2.13) (Sheoran et al. 1990). At a late stage of vegetation, Cd^{2+} did not affect photosynthesis and the enzymes studied. A decrease in their activity was observed only at high concentrations of Cd^{2+} (5 mM).

Some authors argue that the main site of Cd exposure is the light phase of photosynthesis (Küpper et al. 2007). However, other researchers found that Cd primarily interferes with the functioning of the CO_2 assimilation pathway and only then affects the light reactions of photosynthesis (Burzyński and Żurek 2007). Baszyński et al. (1980) showed that the main cause of the decrease in photosynthesis after exposure to Cd is a decrease in the content of Chl, which preceded the decrease in the concentration of CO_2.

Studying the effect of Cd on photosynthesis for short periods of time has largely eliminated the indirect effects of the metal, such as Fe deficiency, a decrease in Chl, and the destruction of general cellular metabolism (Burzyński and Żurek 2007). In maize seedlings (*Zea mays* L.), Cd primarily inactivated Rubisco and PEPC and, secondly, changed the electron transfer rate of PSII, that is, Cd affected both stages of photosynthesis; however, the main goal of the toxic action of Cd was Calvin cycle reactions, not PSII (Wang et al. 2009). In sunflower plants under conditions of Cd stress, a reduction in Rubisco activity was observed at a constant F_v/F_m ratio (Di Cagno et al. 2001). This indicates that the process of photosynthesis mainly changes due to the dark phase.

According to most researchers, a decrease in P_N is most likely to occur when Cd acts on the CO_2 assimilation path. It is assumed that Cd primarily inhibits the carbon photoreduction cycle and only then affects the electron transfer in photosystems (Weigel 1985; Krupa and Moniak 1998; Burzyński and Żurek 2007).

15.6.3 Microalgae Photosynthesis

Heavy metals inhibit growth (Dudkowiak et al. 2011) and photosynthesis of algae (Nishikawa et al. 2003). In *Chlamydomonas reinhardtii*, an inhibitory effect of Cd on OEC and a decrease in ETR in both PSs were found (Perreault et al. 2011). A decrease in ETR under the influence of Cd led to a decrease in apparent activation energy (AAE) for all PSII reduction steps. The effect of Cd on OEC correlated with a variation in AAE for all the PSII reduction phases. In addition, AAE to reduce the plastoquinone pool also had an effect on PSI activity. Inhibition of these sites has shown that the OEC activity of PSII and PSI activity are dependent on AAE associated with the transfer of electrons to PSII. In *Chlamydomonas*, Cd inhibits photoactivation of PSII (i.e., the OEC assembly) by competitively binding to the Ca^{2+} main site in PSII (Faller et al. 2005).

The negative effects of Cd on photosystem II are shown in *Scenedesmus acutus* and *Chlorella vulgaris* (Ilangovan et al. 1998). In addition, the inhibitory effect of Cd on OEC activity has been found (Pagliano et al. 2006). However, La Rocca et al. (2009) at 5 ppm Cd did not show signs of a violation of the acceptor side, despite a decrease in the rate of photosynthesis. This conclusion is consistent with the assumption that Cd primarily affects the donor side of PSII.

Koliella antarctica had a rather high sensitivity to Cd. The degree of exposure to Cd depended on its concentration. After 1 ppm Cd treatment, a moderate toxic effect was shown on growth, chloroplast ultrastructure, chlorophyll content, photosynthesis efficiency (F_v/F_m), and ETR in PSII. Treatment with 5 ppm Cd led to a significant reduction in these processes and even to the death of algae cells (La Rocca et al. 2009).

15.6.3.1 Cyanobacteria Photosynthesis

Cyanobacteria rather quickly accumulate a large amount of toxic metals (Les and Walker 1984), which can lead to inhibition of photosynthesis (Dudkowiak et al. 2011). The degree of toxic accumulation of metals by cyanobacteria depends on the species, physiological conditions, and concentration of metal ions in the medium, as well as on the physicochemical properties of the medium, that is, pH and temperature (Les and Walker 1984; Koelmans et al. 1996). At the same time, it turned out that cyanobacterial thylakoid membranes are much more resistant to the effects of Cd^{2+} than in higher plants (Nováková et al. 2004). In *Synechococcus elongatus*, concentrations of 0–100 mM Cd had a rather activating effect on the thylakoid membranes. An inhibition of PSII photochemical activity was manifested only at 1000 mM Cd, while the site of action of Cd^{2+} was probably on the PSII oxidative side. Analogous data were obtained when measuring oxygen evolution. The carboxylation enzyme activity was maintained even at 1000 mM Cd (Nováková et al. 2004).

Cd^{2+} reduced the growth of cyanobacterium *Nostoc muscorum* cells (Dixit and Singh 2015). Growth inhibition occurred as a result of the destruction of cellular components or impaired absorption of nutrients, as well as due to a decrease in enzyme activity and photosynthesis (Thapar et al. 2008). Cd caused disorganization of thylakoids, a change in the proportions of the pigment antenna, and a reduction in the content of Chl, phycocyanins, and Car (Leborans and Novillo 1996; Dixit and Singh 2015), which led to a decrease in photosynthetic activity (Murthy et al. 1989).

Short-term Cd processing reduced O_2 release rate (Dixit and Singh 2015), that is most likely a result of inhibition of OEC, by replacing with cadmium of divalent cations responsible for water oxidation (Šeršeň and Kráľová 2001; Peters and Chin 2003). In addition, the inhibitory effect of Cd^{2+} is directed to the oxidative side of PSII, but before NH_2OH (Verma and Singh 1995).

At a low concentration (25 µg mL^{-1}), Cd^{2+} inhibits energy transfer on the way to the PSII center, and also causes a conformational modification in the Chl antenna in cyanobacteria (Singh et al. 1993). Higher concentrations (100 µg mL^{-1}) of Cd^{2+} can damage the photosynthetic complex (Dixit and Singh 2015).

Cd^{2+} causes the destruction of phycocyanin in the composition of phycobilisomes, which leads to a decrease in the emission intensity (Singh et al. 1993) in *Nostoc muscorum* (Dixit and Singh 2015). A decrease in the number of phycocyanin in *Nostoc muscorum* cells (Dixit and Singh 2015) and in the cyanobacterium *Spirulina platensis* (Murthy et al. 1989) is observed, which indicates a greater ease of decomposition of phycocyanin by Cd than allophycocyanin in phycobilisome.

15.7 Protection of the Photosynthetic Apparatus

15.7.1 Oxidative Stress and Antioxidant Systems

High concentrations of Cd can cause oxidative stress in plant cells, although it is not a redox metal (Cho and Seo 2005; Vassilev et al. 2005; Masood et al. 2012; Moradi and Ehsanzadeh 2015). Oxidative stress enhances lipid peroxidation (Chaoui et al. 1997), resulting in impaired membrane permeability, and inhibition of growth, photosynthesis, and normal synthesis of Chl (Mobin and Khan 2007; Masood et al. 2012). Blocking electron transfer in PSII by cadmium leads to the generation of reactive oxygen species (ROS), superoxide anion ($O_2^{\bullet -}$), hydroxyl ($OH^{\bullet}$) radicals, and H_2O_2, the accumulation of which leads to the destruction of the chloroplasts' structure and causes leaf chlorosis (Romero-Puertas et al. 2004; Hasan et al. 2011; Ahammed et al. 2012; Masood et al. 2012; Asgher et al. 2014). Cd causes the accumulation of ROS in all organs, thereby affecting the redox balance of the whole plant (Iannelli et al. 2002; Foyer and Noctor 2005).

Among all components, cell membranes are most sensitive to damage by heavy metals (Singh et al. 2006). Lipid peroxidation, determined by malondialdehyde (MDA) content, can be used as a test to determine the development degree of oxidative stress (Kumari et al. 2010; Gallego et al. 2012). The content of MDA in plant tissue increases under the action of toxic Cd concentrations (Ahammed et al. 2013; Xu et al. 2013). With prolonged exposure to Cd, there is a significant reduction in membrane stability index and in electrolyte leakage (Gonçalves et al. 2007), which indicates a serious damage to the integrity of the membranes (Moradi and Ehsanzadeh 2015).

Since Cd cannot participate in Fenton's reactions, its role in the ROS formation mechanism causing membrane damage is unclear (Rodríguez-Serrano et al. 2009). Possibly, under strong illumination of chloroplasts, Cd causes the formation of triplet forms of chlorophyll in PS antennas, and subsequently singlet O_2 and other types of ROS (Atal et al. 1991).

Under stressful conditions in plants, there is an imbalance between the production and scavenging of ROS. In order to reduce the damaging effect of Cd, various mechanisms have been developed in plants that allow both sequestering the metal and neutralizing the ROS generated by it using special absorbers (Siripornadulsil et al. 2002). Protective strategies include the formation of various antioxidants and the activation of ROS-absorbing enzymes, as well as enhancing sulfur metabolism (Fernández et al. 2013; Choppala and Bolan 2014; Ahmad et al. 2015). One mechanism may be the expression or activation of antioxidant enzymes (Ranieri et al. 2005), including superoxide dismutase (SOD; EC 1.15.1.1), which is involved in the early stages of cell defense. The activity of superoxide dismutase depends on the accumulation of Cd in the tissues, species, and stage of plant growth, as well as the time of exposure to the metal (Sandalio et al. 2001; Shah et al. 2001). Superoxide dismutase decomposes $O_2{\bullet}^-$ into H_2O_2 and O_2 (Hsu and Kao 2007; Gill and Tuteja 2010). The accumulation of hydrogen peroxide is limited to catalase localized in peroxisomes and mitochondria (CAT; EC 1.11.1.6), peroxidases (EC 1.11.1.x), and ascorbate peroxidase in chloroplast (APX; EC 1.11.1.7) (Mishra et al. 2006; Bhatt and Tripathi 2011; Sharma et al. 2012). Nonenzymatic ROS quenchers can be carotenoid pigments (Anjum et al. 2015).

Gillet et al. (2006) showed a marked increase in Mn-SOD, but a decrease in Fe-SOD in Cd-treated plants. Similar reactions to oxidative stress have also been observed in other plants (Vido et al. 2001; Sarry et al. 2006). SOD activation also occurred in *Brassica napus* (Meng et al. 2009) and tomatoes (Ahammed et al. 2013). In yeast, Mn-SOD activation and a decrease in Cu/Zn-SOD activity were observed (Vido et al. 2001). Fe-SOD transcript levels are also induced by Cd (Ahammed et al. 2013). A decrease in SOD activity probably occurs when Fe is replaced by Cd in the Fe-SOD enzyme (Yamakura and Suzuki 1980) or when the accumulation of $O_2^{\bullet-}$ exceeds the SOD's ability to eliminate, and ROS could inactivate the enzyme.

According to some authors, the formation of ROS during Cd-stress occurs as a result of a decrease in the level of glutathione and inhibition of GR, CAT, and APX (Dietz et al. 1999; Romero-Puertas et al. 2004). Indeed, in wheat plants (Ahmad et al. 2009), tomato (Ahammed et al. 2013), rice (Shah et al. 2001), and peas (Sandalio et al. 2001), there is a decrease in CAT activity, sensitive to $O_2\bullet^-$ radicals that lead to enzyme degradation (Cakmak 2000). A decrease in enzyme activity can also occur when it is destroyed by proteases or as a result of photoinactivation (Sandalio et al. 2001).

Contrary to the authors mentioned above, other studies have found an increase in APX activity (Gillet et al. 2006; Ahmad et al. 2009), which can compensate for the decrease in CAT in the presence of Cd. Increased APX activity is shown in *Brassica napus* (Meng et al. 2009), *Vigna mungo* (Singh et al. 2008), tomato (Ahammed et al. 2013), and *Brassica juncea* (Mohamed et al. 2012). Induction of the Cd level of the APX transcript is shown in tomato (Ahammed et al. 2013).

Catalase activity after Cd treatment of plants can also increase (Hasan et al. 2008). Ahammed et al. (2013) observed a Cd-induced increase in the CAT1 transcript level. Experiments with plants with different sensitivity to heavy metals revealed a pattern that catalase activity is always higher in plants resistant to Cd (Cho and Seo 2005).

Under the stress of Cd, a loss of Rubisco activity occurs, which cannot be due to the degradation of the Rubisco protein (Pietrini et al. 2003). An increase in the ROS level is accompanied by oxidation of the Rubisco SH groups, which correlates with a reduction in the photosynthesis rate (Liu et al. 2008). In plant seedlings, the main goals of the toxic effects of Cd are Calvin's cyclic reactions rather than PSII (Krupa et al. 1993). Cd stress initially inhibits the carbon photoassimilation cycle and only then affects the ETR in PSII (Burzyński and Kłobus 2004; Burzyński and Żurek 2007; Wang et al. 2009). On the other hand, the action of ROS formed by Cd leads to a decrease in the content of Chl and Car, which is accompanied by lower light absorption and adversely affects the photolysis of water and ETR (Deng et al. 2014).

15.7.2 S-Metabolism Activation

Cd toxicity can be reduced due to increased S-assimilation due to the involvement of S-metabolism in the formation of the antioxidant system of the cell (Bashir et al. 2015), which protects photosynthesis and supports growth under Cd stress (Asgher et al. 2014). The accumulation of Cd in the tissues of many plants stimulates the absorption of sulfates in the roots (Nocito et al. 2002), which is associated with increased expression of ATP-sulfurylase (EC. 2.7.7.4) (Gill et al. 2012), which catalyzes the activation reaction of SO_4^{2-} by interacting with ATP. In turn, plant photosynthesis also depends on S availability, which affects the efficiency of carboxylation and the stomatal movement (Iqbal et al. 2011), since sulfite reductase (EC 1.8.7.1) is a ferredoxin-dependent enzyme and, along with ferredoxin-NADP$^+$ reductase and nitrite reductase (EC 1.7.7.1), competes for the electrons of the PSI transport chain, especially since ferredoxin-NADP$^+$ reductase is inhibited by Cd (Gillet et al. 2006).

15.7.2.1 Glutathione Production

Glutathione is the main substance for maintaining the redox balance of the cell and is used to remove ROS (Noctor and Foyer 1998). Glutathione reductase (GR; EC 1.8.1.7) catalyzes the conversion of oxidized glutathione (GSSG) to reduced glutathione (GSH) (Noctor et al. 2002). The high solubility and mobility of glutathione allows it to be present in large quantities in all cellular organelles (Foyer and Rennenberg 2000). Glutathione can regulate the activity of photosynthetic enzymes associated with thioredoxin (Schürmann and Jacquot 2000). In addition to chloroplasts, glutathione is also present in mitochondria, where it supports oxidative phosphorylation and the formation of ATP (Hutchison et al. 2000).

GR activity with Cd stress is increased in leaves, but decreased in chloroplasts (Ahmad et al. 2009). High GR activity may support increased GSH/GSSG ratio. Increased GR activity is associated with transcriptional or translational modification (Romero-Puertas et al. 2002). Reduced GR expression in roots can lead to oxidative damage after Cd treatment (Mishra et al. 2006). The accumulation of Cd also leads to a reduction in GR activity in chloroplasts, which has been shown in many plants (Zhang et al. 2003; Pietrini et al. 2003; Ahmad et al. 2009).

Glutathione synthesis occurs after activation of inorganic sulfur due to the ATP-sulfurylase enzyme (ATP-S; EC EC. 2.7.7.4) followed by a cascade of enzymatic reactions (Leustek 2002; Tausz et al. 2004). Increased activity of ATP-S and other S-assimilation enzymes in leaves and chloroplasts under Cd stress (Ahmad et al. 2009) promotes plant resistance to heavy metals (Dominguez-Solis et al. 2001).

Synthesis and reduction of glutathione are highly energy-intensive processes. Sulfate reduction in chloroplasts requires eight electrons per molecule (Leustek and Saito 1999), as well as the presence of NADPH to preserve its reduced form (Noctor et al. 1998). Therefore, in order to increase the availability of GSH for the entire plant, large investments in resources are needed at the expense of other processes.

However, an increased concentration of GSH along with phytochelatins (PCs) seems to be the optimal protective strategy for saving key photosynthetic thiol enzymes from inactivating Cd (Pietrini et al. 2003). Cd-induced oxidative stress stimulates the expression of GSH synthesis genes (Schafer et al. 1998), thereby inducing a progressive increase in GSH concentration (Masood et al. 2012; Silva et al. 2018), which contributes to tolerance to oxidative stress (Pietrini et al. 2003). In addition, GSH makes it difficult to relocate Cd from roots to aboveground organs (Nakamura et al. 2013).

A key enzyme that catalyzes the conjugation of xenobiotics with GSH is glutathione S-transferase (GST; EC 2.5.1.18) (Coleman et al. 1997), whose activity (Skórzyńska-Polit et al. 2010; Gillet et al. 2006) and the transcript level GST1 is upregulated by Cd (Ahammed et al. 2013). Cd is a strong thiol scavenger that creates a sulfate deficiency (Nocito et al. 2002). However, Cd can only be captured by reduced forms of thiols (Ow 1996). In addition, GSH effectively reduces the likelihood of Cd interacting with the thiols of the enzyme catalytic centers and inhibiting their ability to carbon photoassimilate (Pietrini et al. 2003).

Thus, increasing GSH concentrations contribute to minimizing Cd stress (Xiang et al. 2001). The increased GSH content correlates with stress tolerance of plants and provides a mechanism for detoxifying heavy metals (Masood et al. 2012).

15.7.2.2 Phytochelatin Synthesis

Phytochelatins (PCs) in plants are sulfur-containing polypeptides with the structural formula $(\gamma\text{-Glu-Cys})_n\text{-Gly}$. PCs are synthesized from GSH in a sequestration reaction using phytochelatin synthase (EC 2.3.2.15) (Grill et al. 1985, 1989). PC synthesis is induced by the accumulation of Cd in plant cells (Sanità di Toppi and Gabbrielli 1999). PCs chelate Cd with SH groups of cysteine mainly in the root cell walls (Bajguz and Hayat 2009; Bajguz 2010) and thus impede the circulation of Cd in the plant (Bajguz and Hayat 2009; Bajguz 2010) and free Cd inside the cytosol (Grill et al. 1985). By the number of phytochelatins formed, one can judge the degree of development of the heavy metal's stress (Cobbett 2000).

15.7.2.3 Phytocystatin Synthesis

One of the strategies for maintaining photosynthesis in Cd stress is the synthesis of thiol compounds, for example, phytocystatin (PhyCys), which are involved in the regulation of metabolic processes (Eason et al. 2014). PhyCys' protective action under Cd stress extends to photosynthetic machinery enzymes (Rubisco), nitrogen use efficiency, and ROS scavengers enzymes (SOD and APX) (Per et al. 2016), as well as to S-assimilation enzymes to maintain higher levels of Cys and GSH for metal detoxification (Khan et al. 2009). In addition, PhyCys can act as a regulator of proteolysis during plant acclimatization, increasing tolerance to Cd (Per et al. 2016).

PhyCys is part of the cystatin superfamily and is a proteinase inhibitor that regulates proteolytic activity (Martínez et al. 2012; Kunert et al. 2015). In addition to functioning as the regulator of numerous metabolic processes, PhyCys is also involved in the formation of plant response to stress (Zhang et al. 2008). PhyCys gene expression (CsC and AtCYS1) was observed during cold and heat stresses, wounding, salinity, and drought (Pernas et al. 2000; Hwang et al. 2010). Overexpression of the AtCYS1 gene led to the prevention of cell death due to exposure to ROS (Belenghi et al. 2003). Overexpression of the BoCPI-1 protease inhibitor delays Chl destruction (Eason et al. 2014). Overexpression of PhyCys delays the destruction of the photosynthetic apparatus during senescence and significantly increases the amount of Rubisco protein (Prins et al. 2008). Ectopic expression of oryzacystatin enhances shoot branching and the accumulation of Chl in leaves (Quain et al. 2014).

15.7.3 Selenium Treatment

Selenium (Se) is not a necessary nutrient, but it can reduce the amount of free radicals in cells and thereby weaken the toxicity of Cd (Lazarus et al. 2006). The presence of Se prevents the absorption of Cd, neutralizes its toxicity, and activates antioxidant enzymes, thereby improving plant growth (Filek et al. 2008). The addition of Se to in vitro wheat cultures significantly improved the development and functioning of chloroplasts and reduced their degradation (Filek et al. 2009), as well as weakened Cd inhibition of photochemical processes (Filek et al. 2010).

Apparently, Se accelerates ETR in PSII, including antennas, which increases the number of active reaction centers and also affects the activity of OEC. By stimulating photosynthesis, Se helps maintain starch concentration, which decrease when exposed to Cd. Adding Se also reduces ROS formation (Filek et al. 2010).

15.7.4 Silicon Treatment

Silicon (Si) fertilization helps to mitigate abiotic stresses due to dilution effects, which leads to increased crop yields (Marschner 1995; Balakhnina et al. 2012). Deposition of Si in the leaves promotes tolerance to Cd, and also contributes to the preservation of water in the cells (Hattori et al. 2005).

A high Si content enhances plant resistance to stress through the activation of protective mechanisms (Mitani et al. 2009). The mechanism for reducing the toxicity of Cd with Si includes a decrease in the solubility of metals due to pH changes, the accumulation of phenols, and the formation of insoluble Cd–Si complexes (Gu et al. 2011). The degree of positive influence of Si during Cd pollution is dependent on plant species (Lukačová Kuliková and Lux 2010).

The addition of Si can alleviate the negative effects of Cd (Kaya et al. 2009; Broadhurst et al. 2013). Adding Si does not increase the production of net dry masses in normal conditions (Silva et al. 2017). However, it has been shown that under Cd stress conditions with prolonged exposure to Si, the net dry masses production increases (Zhang et al. 2008; Rizwan et al. 2012; Silva et al. 2017).

Suppression of absorption and transport of Cd, including through interaction with Si (Farooq et al. 2016), is considered as an effective protective mechanism against the toxic effects of Cd (Song et al. 2009). Adding Si to the soil reduces the availability of Cd, which reduces its absorption (Silva et al. 2017) and more effectively sequesters Cd in the roots (Vaculik et al. 2009, 2012), and also significantly reduces its movement into shoots (Song et al. 2009; Rizwan et al. 2012). Plant hyperaccumulators absorb Si using energy-dependent carriers (Ma et al. 2006). Silicon is able to integrate into the structure of the cell wall, which prevents the absorption of Cd by the roots and its movement into the aboveground organs (Lukačová et al. 2013). When transported to shoots, Si accumulates in the vascular system of the leaves in the form of a polymer, which prevents the movement of toxic ions (Mitani et al. 2005) and contributes to their coprecipitation (Gu et al. 2011). Apparently, Si hinders the transfer of Cd along the apoplastic pathway and contributes to its accumulation in the symplast (Ye et al. 2012).

Silicon can stimulate photosynthesis under conditions of cadmium stress by increasing φP_0 and Φ_{PSII}, decreases F_0, and increases F_v/F_m and qP (Nwugo and Huerta 2008; Feng et al. 2010). The Si use after the Cd stress onset can restore damage to the photosynthetic apparatus and improve Φ_{PSII} (Farooq et al. 2016), which is apparently not associated with a decrease in the content of Chl (Nwugo and Huerta 2008). Chl concentrations do not always change when Si is used under Cd stress conditions (Lukačová et al. 2013), although Feng et al. (2010) observed a higher Chl content with less damage to the thylakoid membranes on cucumber plants.

It should be noted that the Si-dependent blocking of the absorption and transport of Cd from the roots to the aboveground organs is not able to answer the question of why photosynthesis is restored after the end of Cd stress, although the concentration of Cd in the leaves did not change significantly. Apparently, the positive effect of introducing Si into aboveground tissues of the plants is due to the local effects of Si accumulation in the shoot, rather than the effect on Cd transport over long distances (Farooq et al. 2016).

Si-mediated metal stress tolerance also appears to be associated with improved antioxidant activity and high levels of ascorbate and glutathione (Ma and Yamaji 2006). On the other hand, the use of high doses of Si can cause an imbalance of nutrition and reduce the formation of dry matter in plants (Araújo et al. 2011). Si at high concentrations is likely to coprecipitate metals necessary for the functioning of photosynthesis, such as Fe and Cu (Gu et al. 2011).

Thus, the positive effects of Si under Cd stress can be accomplished through several mechanisms, namely, reducing Cd absorption and translocation, improving Cd compartmentation, retuning redox homeostasis, and increasing antioxidant capacity (Farooq et al. 2016).

15.7.5 Brassinosteroid Treatment

Brassinosteroids (BR) are polyhydroxysteroid phytohormones originally found in pollen from *Brassica napus* (Vardhini and Anjum 2015), but then they were found to be widespread throughout the plant because BRs are nontoxic, rapidly absorbed, and metabolized (Bajguz and Tretyn 2003). The classification of brassinosteroids consists in counting the number of carbon atoms in the molecular structure (C27, C28, or C29). Currently, more than 60 BRs have been identified (Haubrick and Assmann 2006), of which 24-epibrassinolide (EBR), 28-homobrassinolide, and brassinolide are biologically active (Vardhini and Anjum 2015).

Brassinosteroids are involved in the regulation of many processes at different levels of plant organization, including growth and productivity (Rao et al. 2002; Sasse 2003), gas exchange (Farooq et al. 2009), antioxidant enzymes (Sharma et al. 2010), and stimulation of chlorophyll synthesis (Fariduddin et al. 2003). In *Arabidopsis*, brassinosteroids stimulated plant growth, inducing cellulose formation, due to overexpression of its synthesis genes (Xie et al. 2011).

BRs participate in developing tolerance to various stresses (Vardhini et al. 2006; Hasan et al. 2011; Ahammed et al. 2012), such as high or low temperatures (Hayat et al. 2010a), moisture stress, drought (Yuan et al. 2010), salinization (Anuradha and Rao 2001; Alyemeni et al. 2013), damage by pesticides, polycyclic aromatic hydrocarbons (Ahammed et al. 2012), and Cd stress (Allagulova et al. 2015).

Brassinosteroids remove the negative influence of Cd stress in plants (Hasan et al. 2008, 2011; Ahammed et al. 2013). The use of BR mitigated the toxicity of Cd for plant growth (Anuradha and Rao 2009; Hayat et al. 2014; Santos et al. 2018). Treatment with EBR under Cd stress enlarged the relative water content in plants (Anuradha and Rao 2009; Hayat et al. 2007). BR reduced Cd in rapeseed plant tissue (Janeczko et al. 2005), cowpea plants (Santos et al. 2018), bean (Rady 2011), wheat (Kroutil et al. 2010), and *Chlorella vulgaris* (Bajguz 2000). EBR is likely to increase phytochelatin production in stress tissue cells (Bajguz 2011). This effect of EBR directly affects the decrease in values of the bioconcentration factor (BCF) and the translocation factor (TF), as well as the decrease in the rate of Cd translocation to the aerial organs (Santos et al. 2018).

Brassinosteroids can mitigate Cd exposure by improving the P_N of plants (Hayat et al. (2010b) by increasing g_s (Zhang et al. 2014). EBR increased the E of plants susceptible to Cd toxicity and simultaneously contributed to water absorption and root elongation (Santos et al. 2018). The increment in water-use efficiency in plants treated with EBR is inextricably related to the increase in the P_N and E (Santos et al. 2018). P_N/C_i values increased in EBR-treated *Vigna unguiculata* as a result of an increase in P_N and a synchronous decrease in C_i (Santos et al. 2018). An increase in the P_N/C_i ratio showed that EBR acted on Rubisco and enhanced CO_2 photoassimilation (Wahid et al. 2008).

EBR facilitated the effects of Cd treatment on the levels of other nutrient metals in plants, which reduced impairment of ionic homeostasis in tissues (Saidi et al. 2013). In *Vigna unguiculata*, EBR maintained the concentrations of Fe and Mn required for Chl biosynthesis (Lopes Júnior et al. 2014). EBR mitigated the toxic effects of Cd, contributing to an increase in Chl *a* and *b* in *Vigna* (Santos et al. 2018), Chl *b* in *Phaseolus* (Rady 2011) and total Chl in *Brassica juncea* (Hayat et al. 2007) and radish plants (Anuradha and Rao 2009).

BR mitigates the negative effects of Cd on fluorescence parameters, primarily by preventing the RC destruction and supporting TR_0/CS and ET_0/CS. The stimulatory effects of BR on F_v/F_m have been observed under various adverse conditions, namely, phenanthrene and pesticide contamination, as well as cooling (Cui et al. 2011). The EBR use in rape seedlings reduced the effects of inhibiting photochemical processes caused by Cd, reducing damage to photochemical RC and OEC, and also supporting efficient transport of the photosynthetic electron. EBR enhanced TR_0/CS, ET_0/CS, and φP_0, as well as Ψ_0. EBR limited the Cd-induced increase in dissipation of excitation energy (DI_0/CS), while at the same time protecting the OEC complex from a decrease in activity (Janeczko et al. 2005).

EBR mitigated the negative actions of Cd in the light phase of photosynthesis in plants *Vigna unguiculata* (Santos et al. 2018), *Triticum aestivum* (Hayat et al. 2014), *Phaseolus vulgaris* (Wael et al. 2015), and *Carthamus tinctorius* (Moradi and Ehsanzadeh 2015), minimizing negative effects on F_0, F_m, and F_v/F_m. Janeczko et al. (2005) revealed an increase in F_m after EBR treatment of plants subjected to Cd stress. However, with a high Cd concentration in *Zea mays*, a decrease in F_m values was observed (Wang et al. 2009). The use of EBR led to an increase in Φ_{PSII} and qP values in Cd-treated plants, which indicates an increase in photon absorption for use in photochemical reactions and an improvement in the ability of plants to absorb excitation energy in PSII reaction centers (Santos et al. 2018).

Epibrassinolide attenuates NPQ and the amount of excess energy of photosystem II in Cd-treated plants, thereby reducing thermal dissipation associated with excitation energy (Santos et al. 2018). This indicates an excessive excitation of photosystem II with an excess of light. In this case, excess energy can be eliminated by quenching to exclude the destruction of photosystem II (Silva et al. 2012). In plant photosystems, under the Cd influence, the electron transport rate decreases (Silveira et al. 2015). According to Santos et al. (2018), EBR treatment mitigated the negative effects of Cd on the ETR by increasing the redox efficiency of PQ.

Epibrassinolide treatment significantly increases photosynthetic assimilation of CO_2 (Anuradha and Rao 2009; Ahammed et al. 2012), contributing to an increase in dry weight of the plant (Hayat et al. 2000; Yu et al. 2004). BR increases the Chl content (Hayat et al. 2012), apparently as a result of the expression of genes synthesizing these pigments (Bajguz 2011). Epibrassinolide stimulates the activity of photosynthesis both by expressing genes and by increasing the enzyme activities of the Calvin cycle (Jiang et al. 2012).

In plants under Cd stress, a sharp reduction in the activity of carbonic anhydrase (EC 4.2.1.1) occurs (Anuradha and Rao 2009), which catalyzes the invertible conversion of HCO3 and CO_2 and thereby is able to regulate the CO_2 applicability for Rubisco (Badger and Price 1994). However, enzyme activity can be restored using EBR.

The molecular defense mechanism of photosynthetic reactions using EBR may enhance the activities of antioxidant systems (Rady 2011; Mazorra et al. 2002), which limit the development of Cd-induced oxidative stress (Ahammed et al. 2013). The use of EBR can reduce the content of ROS and MDA in affected plants, that is, BR can alleviate the effects of Cd stress (Hasan et al. 2008, 2011; Ahammed et al. 2012, 2013). Treatment with epibrassinolide reduces electrolyte leakage that occurs after treatment of plants with Cd (Allagulova et al. 2015; Santos et al. 2018). The decrease in oxidative stress is due to BR-induced enhancement of antioxidant activity and subsequent uptake of ROS (Cui et al. 2011).

Epibrassinolide increases the activities of glutathione S-transferase, peroxidase, and GR (Ahammed et al. 2012). The use of EBR under Cd stress can significantly increase the transcription of antioxidant enzyme genes (Ahammed et al. 2012, 2013). An increase in the activities of these enzymes can occur both by stimulating gene expression in de novo synthesis and by activating existing enzymes in response to BR treatment (Cui et al. 2011). Pretreatment of EBR radish seeds contributed to an increase in nitrate reductase activity under stress Cd (Anuradha and Rao 2009).

In addition, EBR treatment leads to the induction of secondary metabolism enzymes and also enhances their catalytic activity (Ahammed et al. 2013). The increased activity of phenylalanine ammonia lyase may contribute to the accumulation of phenols and flavonoids (Dixon and Paiva 1995), which can detoxify ROS (Wang et al. 2011). Activation of cinnamyl alcohol dehydrogenase means an increase in the cinnamic alcohol formation involved in the lignification process (Mitchell et al. 1994).

The efficiency of the protective effect of EBR increases in older tissues (Janeczko et al. 2005). This phenomenon may be due to a correlation between the increase in Cd toxicity and tissue age or the effects of heavy metals for a long time (Krupa and Moniak 1998). In plants subjected to simultaneous exposure to EBR and Cd, ETR/P_N value decrease, indicating that Mehler's reaction, photorespiration, and CO_2 assimilation used less photochemical energy (Fang et al. 2011). The ETR/P_N ratio can reflect the power of alternative electron sinks (Silva et al. 2010) and is used as a criterion for the rate of photorespiration as a defense system (Palliotti et al. 2015).

15.7.6 Decrease in Cd Toxicity Under Salt Stress

The effect of Cd on photosynthesis reactions can be largely indirect due to functional changes in other physiological processes (Burzyński and Kłobus 2004), for example, due to impaired absorption and distribution of nutrients (Krupa et al. 2002) and induction of ROS (Dietz et al. 1999). The disturbance of water metabolism observed in Cd stress (Poschenrieder and Barceló 1999) leads to an increase in stomatal resistance (Baryla et al. 2001) and, consequently, CO_2 absorption (He et al. 2008; Asgher et al. 2014). A decrease in the concentration required for the assimilation of intracellular CO_2 may lead to a decrease in the photosynthetic activity (Shi and Cai 2008; Ahammed et al. 2013; Xue et al. 2018).

The effect of Cd on photosynthesis occurs due to a change in the activity of reactions of the light and dark stages, as well as a decrease in the rate of Chl synthesis (Ebbs and Uchil 2008), and also by reducing the amount of the oxygen evolving complexes (Janeczko et al. 2005). The negative effects of Cd on Rubisco as the main CO2 fixation enzyme have been shown (Ishida et al. 1999).

The study of the effect of different concentrations of Cd in solution on wheat seedlings lacking the root system made it possible to exclude the effect of the root conducting system on metal absorption. Our studies have shown that Cd reduces the rate of photosynthesis (Table 15.1). The introduction of Cd into the solution caused a reduction in the ETR of chloroplasts, the maximum rate and efficiency of the carboxylation reaction, and the rate of utilization of triose phosphates.

Changes in the physiological parameters of the leaves were observed for 4 days using high (0.1 mM) and ultrahigh (1 and 5 mM) concentrations of Cd^{2+}. The use of 0.1 and 1 mM Cd^{2+} led to a gradual decline in the relative water content and Chl content in the leaves, as well as in the rate of photosynthesis, as assessed by the photosynthetic O_2 evolution rate (Figs. 15.1–15.3). At ultrahigh concentrations (5 mM) of Cd^{2+}, a significant decrease in photosynthetic activity occurred already during the first hours after treatment with Cd.

The violation of water metabolism of plants under the action of Cd occurred simultaneously with a decline in the water content in the leaves, which is very similar to the process observed at salinity. The simultaneous presence of Cd in a 50 mM NaCl solution led to the activation of anti-stress defense mechanisms. The presence of NaCl in solutions with a high concentration of Cd^{2+} (0.1 and 1 mM) had a paradoxically positive effect on the photosynthetic O_2 evolution rate. In the first 6 h of incubation, a sharp decrease in photosynthetic activity occurred. Subsequently, the rate of O_2 release in the presence of Cd + NaCl exceeded that of plants with one Cd (Fig. 15.1a, b), which may be due to the inclusion of protective mechanisms. The mechanism of this phenomenon is not yet clear. Given the rapid response of plants, it is possible that Na^+ has a direct effect on the oxygen evolving complex PSII, removing the inhibitory effect of Cd. The addition of NaCl had no noticeable effect on the relative content of water and Chl in the leaves of the plants, although their content decreased during the experiment (Figs. 15.2 and 15.3). The extremely high concentration of Cd^{2+} (5 mM) caused a rapid irreversible decline in photosynthetic activity despite the presence of NaCl (Fig. 15.1c).

Table 15.1 The P_N/C_i curve parameters of *Triticum aestivum* seedlings treated with 0.1 mM Cd^{2+}

Parameters	Control	0.1 mM Cd
The maximal rate of CO_2 uptake, μmol CO_2 m^{-2} s^{-1}	5.96 ± 0.22	3.84 ± 0.12
Rate of nonphotorespiratory CO_2 efflux in the light, μmol CO_2 m^{-2} s^{-1}	0.41 ± 0.02	0.46 ± 0.02
Efficiency of carboxylation, μmol CO_2 m^{-2} s^{-1} Pa^{-1}	0.17 ± 0.01	0.13 ± 0.01
The maximal rate of a carboxylation, μmol m^{-2} s^{-1}	6.15 ± 0.26	4.0 ± 0.22
Rate of electronic transport at a light saturation, μmol m^{-2} s^{-1}	15.9 ± 0.81	7.6 ± 0.32
Rate of recycling triosophosphates, μmol m^{-2} s^{-1}	1.27 ± 0.08	1.1 ± 0.05

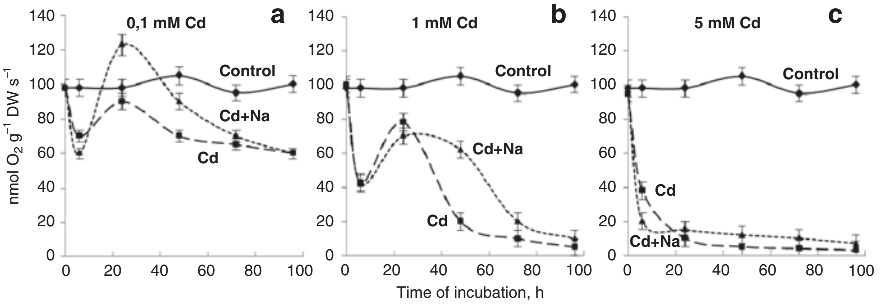

Fig. 15.1 Photosynthetic release of O_2 during incubation of wheat seedlings in Cd^{2+} solutions of various concentrations with the addition of 50 mM NaCl

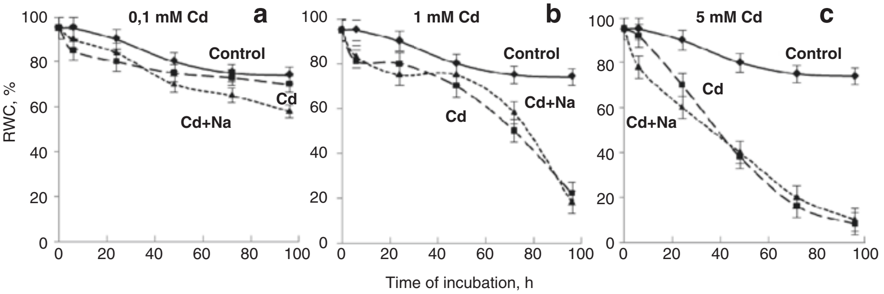

Fig. 15.2 Relative water content (RWC) of wheat seedlings in Cd^{2+}solutions of various concentrations with the addition of 50 mM NaCl

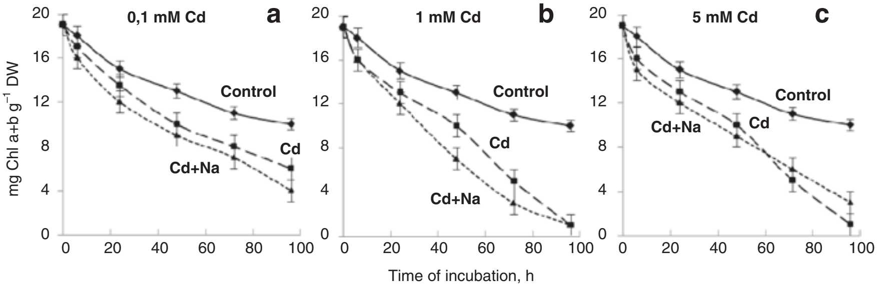

Fig. 15.3 The total chlorophyll content in leaves of wheat seedlings in Cd^{2+}solutions of various concentrations with the addition of 50 mM NaCl

15.8 Cd Effect on C-Metabolism

The carbohydrate metabolism of plants directly depends on the activity of the photosynthetic apparatus and its inhibition in the presence of Cd (Weigel 1985; Baszyński 1986). In the shoots of rice plants under the influence of Cd, the total content of carbohydrates increases, and the distribution of assimilates between organs also changes. Carbohydrate content increases in the stem and leaves, but remains unchanged in the roots (Moya et al. 1993). Large amounts of starch also accumulated in the cells of the microalga *Koliella antarctica* (La Rocca et al. 2009). Perhaps this is due to a sharp suppression of growth and a decrease in the nutritional need of cells (La Rocca et al. 2009). In contrast, sugar beet roots and shoots showed a decline in sugar after exposure to Cd (Greger and Bertell 1992).

In rice seedlings, treatment with 0.1 mM Cd blocked the movement of stored carbohydrates from seeds to the rest of the plant (Moya et al. 1993). A decrease in transport speed may result from the slowdown in several transport processes, including loading, transferring, and unloading (Samarakoon and Rauser 1979). A larger upbuilding of carbohydrates in the seeds may be associated with a lesser loading in the source areas. Blocking the movement of stored carbohydrates and reducing unloading in the final tissue explain the accumulation of substances in the stem, but not in the root.

On the other hand, the accumulation of carbohydrates may be associated with an increase in the glyoxylate pathway under the conditions of disturbance of the dark reactions of photosynthesis in Cd-treated plants. Indeed, under these conditions, the activation of glyoxylate pathway enzymes, namely isocitrate lyase and malate synthase, has been shown (Gillet et al. 2006). An increase in the activity of one of the glycolysis enzymes, phosphoglycerate mutase, was also noted. However, due to the reversibility of the reaction, under conditions of Cd stress, this enzyme is apparently involved in the process of gluconeogenesis and the synthesis of sugars from acetate.

Under conditions of Cd stress, a significant accumulation of starch occurred in rape culture (Shukla et al. 2003). In this regard, the reaction of the plant to the presence of Cd is similar to the reaction of photosynthetic plant tissues to darkness. Filek et al. (2010) suggested that starch accumulation may be due to the formation of a starch radical as a result of redox processes induced by Cd, when excess electrons are fixed on the starch polymer matrix.

On the other hand, during starch accumulation, Cd binds to SH groups of fructose 1,6-bisphosphatase in the cytosol, which inhibits the synthesis of sucrose and limits the recirculation of phosphates between the cytoplasm and chloroplasts (Sharkey 1990). Inhibition of P-metabolism enhances starch synthesis. Similar processes occur at high CO_2 or low temperatures in C3 plants (Pietrini et al. 2003).

At the same time, Gillet et al. (2006) observed an increase in uridine diphosphate (UDP)-glucose:protein transglucosylase activity (EC 2.4.1.112) involved in the synthesis of protein-bound alpha-glucan. The enzyme may be associated with reversible glycosylated polypeptides, which are highly conserved plant-specific proteins, which can perform self-glycosylation. This increase may be the reason for the accumulation of starch in Cd-treated plant cells (Nishikawa et al. 2003).

15.9 Cd Effect on N-Metabolism

Carbon dioxide is the final electron acceptor of the transport chain of photosystems. In conditions of CO_2 deficiency, for example, in the case of Cd stress, excess light energy is partially dissipated (Qiu et al. 2003), but can also be used to recover alternative electron acceptors (Eichelmann et al. 2011), for example, NO_2^-, the reduction of which occurs by means of a light-dependent nitrite reductase. Since eight electrons are required for the photoassimilation of each NO_2^- molecule into glutamate, compared to four electrons for CO_2 assimilation (Robinson 1986), photoreduction of carbon dioxide predominates under normal conditions. It would seem that under the conditions of CO_2 limiting under Cd stress, the main flow of the electron transport chain can be redirected to the restoration of alternative electron acceptors. Indeed, a decrease in photosynthetic activity under Cd stress is accompanied by an increase in demand for N-compounds in the plant, which may be due to the participation of N in the regulation of photosynthesis (Marschner 1995). However, in the plant there is a close relationship between C and N metabolism. There is a synchronous decrease in photosynthesis and photosynthetic nitrogen-use efficiency (Khan and Khan 2014). In turn, a correlation was found between the N content and photosynthesis activity (Iqbal et al. 2011), as well as the Rubisco content and S-metabolism (Iqbal et al. 2012). N limiting can lead to a high decrease in the photosynthetic efficiency (Resurreccion et al. 2001). In fact, treatment with high concentrations of Cd reduces the total N content, which leads to an imbalance between C, S, and N metabolism and, as a result, growth inhibition and a decrease in resistance to Cd stress (Gill et al. 2012).

It is assumed that a decrease in nitrogen use efficiency implies a lower N quota appropriated to the photosynthetic apparatus (Takashima et al. 2004). Indeed, in the presence of Cd, a decrease in the activity of nitrate reductase was observed (Anuradha and Rao 2009; Gill et al. 2012), a key enzyme for fixing inorganic N from the soil, reducing NO_3^- to NO_2^-. At relatively high Cd levels (100 μM), is decreased glutamine synthetase activity (Devriese et al. 2001), which catalyzes the synthesis of glutamine from glutamate and NH^{4+}. Gillet et al. (2006) suggested that low glutamine synthetase activity in the cytosol and chloroplasts under Cd stress may be associated with an inhibition at the expression level. Inhibition of glutamine synthetase may contribute to an increase in the level of glutamate required for the biosynthesis of proline, glutathione, and phytochelatins. This assumption is also confirmed by an increase in the activities of methionine synthetase, catalyzing the final stage of methionine biosynthesis, and S-adenosylmethionine synthetase, catalyzing the first stage of cysteine biosynthesis from methionine (Gillet et al. 2006). Cysteine can later be used for glutathione biosynthesis.

As a result of inhibition of photosynthetic activity due to Cd stress, it becomes necessary to obtain ATP from other sources. In this case, enzymatic pathways with a lower consumption of ATP per electron begin to prevail (Eichelmann et al. 2011), which is accompanied by the formation of additional ATP (Noctor and Foyer 1998), which can be used in the synthesis of secondary metabolism substances. In plants at Cd stress, ATP synthase activity may increase, leading to activation of ATP metabolism and consumption (Kalaji et al. 2014). Gillet et al. (2006) found that with Cd stress there is an increased expression of ATPases in various organelles, as well as inorganic pyrophosphatase. Nishikawa et al. (2003) revealed a correlation between P-metabolism and Cd detoxification during vacuolization.

15.10 Proline Accumulation

Cadmium toxicity can also be neutralized by proline accumulation (Siripornadulsil et al. 2002). In fact, the accumulation of nitrogen-containing compounds, including proline, is part of a general strategy for adapting plants to the negative effects of various stresses (Hare and Cress 1997). Cadmium is one of the strongest producers of proline among other heavy metals (Alia 1991). Increased resistance to Cd stress as a result of proline accumulation has been shown in several studies (Shevyakova et al. 2003; Moradi and Ehsanzadeh 2015). Synthesis of proline is carried out with the expenditure of a large amount of energy. However, under stressful conditions, these costs are justified, since in large quantities proline is able to maintain cell homeostasis (Hare and Cress 1997), stabilize the enzyme structure (Demiral and Türkan 2005), enhance membrane stability, and participate in ROS protection (Khan et al. 2007). An increase in the $NADP^+/NADPH$ ratio as a result of proline biosynthesis stimulates the oxidative pentose phosphate pathway and, thus, provides precursors for the production of secondary metabolites (Hare and Cress 1997). In addition, proline can serve as an energy source in the restoration of plants after stress exposure (Hare and Cress 1997).

15.11 Conclusion

Various mechanisms of the toxic effect of cadmium on plant photosynthesis are presented. The action of Cd can be divided into a direct effect on the photosynthetic apparatus in chloroplasts and indirectly, with the participation of various physiological and metabolic processes localized both in the leaves and in other organs of the plant. It is shown that there are many local targets for the action of Cd on the photosynthetic apparatus, which to some extent affect the photosynthesis process, among which it is difficult to single out the main direction of the toxic action of the ion. Accordingly, it is difficult to develop general principles for counteracting Cd toxicity on the photosynthetic apparatus. The most effective way to avoid the effects of

Cd toxicity is to use plant species that are most resistant to the absorption of Cd from the soil. The remaining measures of protection against absorbed Cd are in the process of formation and study of the physiological and biochemical bases of the existing mechanisms. We hope that this review will help solve this problem.

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