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Review Article

IMPACT OF HEAVY METAL POISONING ON CYANOBACTERIAL PHOTOSYNTHESIS AND ITS DETOXIFICATION-A REVIEW

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ABSTRACT

Cyanobacteria is a photosynthetic prokaryote, these obtain their energy through photosynthesis. In this review, we summarize the effect of heavy metals on cyanobacterial photosynthesis and its detoxification. Now a day's metal contamination due to natural and anthropogenic sources is a global environment concern. Metals were affected the photosynthetic process like photosystem II complex, cytochrome b6f complex, photosystem I complex and ATP synthase, photosynthetic energy transfer process in cyanobacteria phycobilisomes. Here it is also mentioned heavy metal induced altered macromolecules metabolism and changes in the central dogma of life (DNA→ mRNA → Protein). And also recent advances have been made in understanding heavy metal-cyanobacteria interaction and their application for metal detoxification.

Keywords: Cyanobacteria, Detoxification, Photosynthesis, Macromolecules

INTRODUCTION

Cyanobacteria are phylum of bacteria, obtain their energy through photosynthesis, this process is a flexible molecular machine. Cyanobacteria contribute about 40% present day global photosynthetic biomass production and its convert solar energy into biomass-stored chemical energy at the rate of ~450 TW. Cyanobacterial electrogenic activity is an important microbiological conduit of solar energy into the biosphere [1]. Heavy metals are disturbed the photosynthetic energy process in Blue Green Algae (BGA) and red algae.

Heavy metal causing toxicity in plants and cyanobacteria, this metallic element which is toxic has a high density (5mg/cm^3), and specific gravity or atomic weight. Heavy metals fall into 2 groups; the 1st group essential metals (Fe, Zn and Cu), these metals function as micronutrients for plants and cyanobacteria. Which are involved in numerous physiological processes and photosynthetic reactions, but at high concentrations they are strongly toxic and impair plant growth and productivity. The heavy metals of the second group include nonessential metals, which are major pollutants of the environment such as Cd, Pb, Hg, As and are very toxic even at low concentrations and for them no biological functions are known [2].

Sources of heavy metals in the environment

Heavy metals are natural components of the Earth's crust. Metals are entering into the environment from natural and anthropogenic sources (Table 1). Anthropogenic activities represent the main source of metal contamination in the environment [3], i.e; mining and smelting of minerals or metals, surface finishing industry, energy and fuel production, fertilizer and pesticide industry, electroplating, electrolysis, electro-osmosis, leather work, photography, manufacture of electrical appliances, aerospace and atomic energy installation, etc. are the major source of heavy metal pollutants. The principal metal emission sources come from the following industries: petrochemical, extractive, and metallurgic (foundry and metallurgy), mechanic (galvanic processes, painting), chemical (paints, enamels, plastic materials) and ceramic [4-6]. Blue-green algae particularly recommended to the bioremediation processes devoted to the degradation (or) recovery of pollutants from contaminated environments.

Table 1: Anthropogenic sources of heavy metals in the earth crust.

Heavy metal	Sources	Reference
As	Pesticides and wood preservatives	[7]
Cd	Paints and pigments, plastic stabilizers, electroplating, incineration of cadmium-containing plastics, phosphate fertilizers.	[8,9]
Cr	Tanneries, steel industries, fly ash	[10]
Cu	Pesticides, fertilizers	[11]
Hg	Release from Au–Ag mining and coal combustion, medical waste	[6]
Ni	Industrial effluents, kitchen appliances, surgical instruments, steel alloys, automobile batteries	[12]
Pd	Aerial emission from combustion of leaded petrol, battery manufacture, herbicides and insecticides	[7,8]

Metal toxicity may result in decreased light harvesting pigments, nutrient imbalance, increasing antioxidant enzymatic activity and induction of oxidative stress it leads to inhibition of photosynthetic process in algae/cyanobacteria, changes in morphology have also been reported [13, 14]. Growth inhibition and chlorosis are common symptoms of metal toxicity, in which, photosynthesis is the most affected metabolic process in higher plants and Blue-green algae [15].

Heavy metal impact on higher plants

Higher concentrations of many heavy metals severely damage to physiological mechanisms in higher plants includes, disruption of many physiological functions by binding to protein sulfhydryl groups and substituting essential ions [16]. The stressful conditions of the environment such as water stress, soil salinity, heat, chilling, an aerobiosis, pathogenesis, wounding, gaseous pollutants, heavy metals, etc. drastically affect plant growth and metabolism and in turn limit crop productivity. Several studies have been done to understand heavy metal effect on photosynthetic electron transport [17]. Leaf chlorosis in plants grown on metal-polluted soil can be due to a low chloroplast density caused by a reduction in the number of chloroplasts per cell and a change in cell size, suggesting that the excess of metal interferes with chloroplast replication and cell division [18].

Heavy metals have multiple effects in the plant cytoplasm:

- They can bind to functionally essential SH-groups in enzymes and thereby inactivate them.
- They can substitute functional elements in prosthetic groups of enzymes resulting in an inactive catalysis. This is particularly the case for cadmium substituting zinc in proteins.

Heavy metal impact on Morphology of cyanobacteria & cyanobacterial photosynthesis

Cyanobacteria are major biomass producers in aquatic ecosystems and represent more than 50% of the biomass in several ecosystems. Photosynthetic organisms are highly sensitive to heavy metal ions. Bioaccumulation of heavy metals like mercury (Hg), lead (Pb), and cadmium (Cd) by cyanobacteria, *Nostoc muscorum* and *Synechococcus* PCC 7942 and their effects on photosynthetic pigment content, laser induced chlorophyll fluorescence and PS II-based electron transport and antioxidant activities were determined. Cyanobacteria are oxygen-evolving organisms that respond to stress conditions such as light deprivation. Cyanobacterial growth inhibition and chlorosis are common symptoms of metal toxicity, in which, photosynthesis is the most affected metabolic process [15]. Changes in morphology have also been reported [14]. Metals can penetrate into unicellular organisms through the whole surface of the cell.

Thylakoid membrane

Lipids are necessary for maintaining the structural integrity of membranes and constitute approximately 40% of the total dry weight of membranes, the remaining 60% being proteins [19]. Several of the heavy metals are known to affect the thylakoid membranes both structurally and functionally. Damage to the cellular membranes, especially for the plasma membrane, is one of the primary events in heavy metal toxic effects in plants [20]. Heavy metals disrupt cellular membranes resulting in the conversion of unsaturated fatty acids into small hydrocarbon fragments such as malondialdehyde. Metal ions can also replace calcium ions at its essential sites on the membranes. Furthermore, plant plasma membrane is dynamic and its lipid composition/structure is changed with variations in the external environment. Plasma membrane changes might have an adaptive value or injuriously affects membrane properties and functions [21, 22].

Energy transfer

Photosynthetic energy transfer process within the phycobilisomes can be influenced by several environmental factors; such as, low temperature, high temperature [23, 24, 25], heavy metals [17] salt stress [26] and state transition [27].

Effect of heavy metal toxicity on macromolecules

The excess ROS react with biomolecules such as lipids, nucleic acids and proteins hence lead to the altered fluidity of membrane, loss of enzyme function and genomic damage [28, 29]. The total protein content, total carbohydrate and the total free amino acids of the tested green alga *Chlorella vulgaris* gradually decreased in a manner dependent on the metal concentration in the medium. The total carbohydrates content of *Chlorella* cultures grown seven days under various concentrations of cobalt, copper and zinc were also determined. The carbohydrate content of the tested alga also declined in a manner dependent on the metal concentration exist in the medium, but the inhibitory effect of the three tested metals was not pronounced as on protein content.

Carbohydrates

Effect of HM on glucose, sucrose, sugars Metabolism and Bioremediation process Reddy et al., [30] studied the effect of Mercuric chloride Carbohydrate metabolism of freshwater mussel Parreysia. UDP-glucose is not only a necessary metabolite for cell wall biogenesis, but it is involved in the synthesis of the carbohydrate moiety of glycolipids and glycoproteins [31].

Amino acids and Proteins

Heavy metal (Hg, Pb and Cd) salts act to denature proteins. Proline is an extensively studied molecule in the context of plant responses to abiotic stresses. Many plants accumulate this compatible solute under water deficit [32], salinity [33], low temperature [34], high temperature, and some other environmental stresses. When compared at equal toxic strength, proline accumulation decreased in the order Cd > Zn > Cu [35].

Membrane

Mercury (Hg), Pb, Zn, Ni, Cu and Cd metal ions to disturbances the structure of cell membrane in animal/microorganism. Since lipid and protein molecules are located in close proximity in biological membranes, their different mobilities inevitably give rise to frictional forces at the colliding molecular interfaces. The motional gradient between proteins and lipids leads to the formation of a solvation shell of lipids around the proteins. In this shell, lipids are restricted in their motions with respect to the fluid bulk lipids [36].

Lipids

Photosynthesis is generally accepted that heavy metal-induced damage is manifested either via an increased lipid peroxidation or via distorted proteins [37]. Metal contamination seriously affects the concentrations of the major storage compounds trebalose, glycogen, and lipids.

Nucleic acids

Heavy-metal toxicity in our environment arises in part from the covalent interactions of heavy-metal ions with nucleic acids. Heavy metal ions (Zn^{2+} and Cd^{2+}) were inhibited the transcription process initial activator Sp1 factor [38]. In addition, these heavy metals interfere with metalloregulatory proteins and in so doing disrupt gene expression [39]. Metal ions and complexes associate with DNA and RNA in a variety of ways. The genes under this metal-dependent control encode a variety of proteins involved in the cellular homeostasis of both essential and toxic metals.

Effect of heavy metal ions on general photosynthesis:

Photosynthesis, an important process for plant growth and biomass production is negatively affected due to increasing levels of heavy metals in air emissions or soil environment [40]. Heavy metals are generally inhibiting normal physiological processes and also disturbances the photosynthetic process in cyanobacteria and higher plants (Table 2). It has previously been shown that different heavy metals can interfere with various steps of the photosynthetic electron transport chain. Inhibitions were found on both the donor and acceptor sides of photosystem II (PS II), at the cytochrome b_6f complex and in photosystem I also. In the photosynthetic electron transport chain, photosystem (PS) is the site most sensitive to metal ions [41].

Photosynthetic pigments

Reduction of photosynthetic pigments by the heavy metals also indirectly influences the photosynthesis. *Chlorella* was grown with Zn, for this study chlorophyll *a*/b content totally decreased. Influence on photosynthetic activity and pigment content was in some cases observed [42]. Phycobilisomes are attached to the cytosol (stromal) face of the cyanobacterial thylakoid membrane. PBsomes are large water-soluble protein complexes which usually consist of a tri cylindrical allophycocyanin (APC) core and six phycocyanin (PC) rods attached to the core [43]. PBsomes are structurally related to mammalian bile pigments. Heavy metal toxicity causes reduction of leaf growth and disorganization of chlorophyll structure [44]. Interaction of Heavy metals with light harvesting pigments (chlorophyll, carotenoids) reduces their content [18-45] and disrupts energy transfer in light-harvesting antennae. Metals are damaging the structure and function of the chlorophyll a [46]. Photosynthetic pigments were found to be reduced under the excessive concentrations of Hg [47], Cu [48], Cr [49], Ni [50], Cd [51].

Effect of heavy metal toxicity on PS II

The photosynthetic apparatus including photosystem II (PSII) is particularly sensitive to heavy metals [52]. Though both Cu at an equimolar concentration to PSII RC [53]. Electron transport between Pheo and Q_A was impaired in PSII core and RC particles by Cu (80 mM) treatment [54]. Yruela et al., [55] showed that <230 Cu (II) or PSII RC, which inhibited O_2 evolution and variable chlorophyll a fluorescence around 50%, did not affect the polypeptide composition of PSII, and only higher copper concentration (300 mM, Cu(II)/PSII RC ¼ 1400) caused the release of OEC polypeptides. Thermo luminescence measurements identified the electron transport between Q_A and Q_B as the site of action of Ni, Zn, and Co in isolated thylakoids [56]. It catalyses the light-driven reduction of plastoquinone by electrons from water which is oxidized to molecular oxygen [57]. Heavy metals are known to interfere with a variety of photochemical functions at multiple sites [58].

Table 2: Metals toxic effects in photosynthetic process of cyanobacteria/ plant

Metal	Toxic Effects	Reference
As	As (as arsenate) is an analogue of phosphate and thus interferes with essential cellular processes such as oxidative phosphorylation and ATP synthesis	[59]
Cu	Disturbance in the thylakoid membrane functions and chloroplast structure	[45]
	Inhibits photosynthetic electron transport activity on both PSI and PSII	[60]
Fe	Impairs photosynthetic electron transport Induces oxidative stress	[61]
Mn	Reduces activity of RUBP carboxylase Inhibits chlorophyll biosynthesis Reduces net photosynthetic rate (PN)	[62]
Ni	Inhibit seed germination, plant growth, mitotic activities,	[63]
	Chlorophyll degradation, chlorosis, necrosis and wilting & interfere with photo-system activity	[64]
Zn	Decreases total chlorophyll content and Chl a/b ratio	[65]
	Inhibits CO_2 assimilation; Decreases activity of oxygen evolving compelex (OEC); disturbances the Calvin cycle and photosystem activities	[66] [67]

The PS II supported electron transport activity is more susceptible to heavy metal like Cr [68]. Horcsik *et al.*, [69] showed the alteration in PS II photochemistry in heavy metal (Cr) treated green algae. Under *in vitro* conditions, the above-mentioned donors are unable to restore the PS II activity [15]. The above studies indicate that PS II reaction center could be the target for heavy metal action [15]. Excess concentrations of HM impact electron transport on the acceptor side of PS II and may inhibit electron transport between PSII and PSI due to the effects on membrane lipids [70]. Some researchers have reported to a photosynthetic functional complex of photosystem II was very sensitive to Cd^{2+} ions.

Water splitting complex

The loss of PS II catalyzed electron transport activity is due to the alterations in the water oxidation complex (WOC) [15]. PS II activity undergoes gradual decrease because of the destruction of D1 protein of PS II under Cr stress [71- 15].

Effect of heavy metal toxicity on PS I

The inhibitory effect of metals on reducing side of PSI electron transport system has been reported in algae and plants by various authors. Photosystem I catalyzed electron transport is less sensitive compare to that of PS II. PS I activity can be affected at the oxidizing site of Hg. Other possible sites for inhibition of Hg are reaction center of PS I, Fd, FNR and Fe-S centers [72-73].

Effect of heavy metal toxicity on Cytochrome b_6f Complex

The Cyt b_6f complex has also been suggested as an inhibitory site. The electron transport activity is also decreased due to the substitution of heavy metal in PCy and Cyt b_6f complex Cu: [74]; Ag: [75].

Effect of heavy metal toxicity on ATP synthase

According to the literature, chloroplast of ATP synthase/ATPase activity is decreases under Cd^{2+} ion toxicity [76].

Effect of heavy metal toxicity on photosynthetic enzymes

Chlorophyll biosynthetic enzymes of photochlorophyllide reductase under heavy metal toxicity [77], ALA dehydrogense [78]. Inhibition of enzyme activity by the low or high concentration of metal ions i.e, Hg, Pb, Zn, Ni, Cu and Cd. From *in vitro* experiments, at least two potential metal sensitive sites can be derived in the photosynthetic electron transport chain: the water splitting enzymes at the oxidising side of PSII and NADPHoxidoreductase at the reducing side of PSI [65].

Effect of heavy metal on photophosphorylation

Under heavy metal stress between two types of phosphorylations, non cyclic phosphorylation was more susceptible than cyclic phosphorylation [79]. But under Cu stress both phosphorylations were inhibited at relatively under high concentrations.

Molecular targets of heavy metal toxicity

Certain forms of the heavy metals arsenic and chromium are considered human carcinogens, although they are believed to act through very different mechanisms. Chromium (VI) is believed to act as a classic and mutagenic agent, and DNA/chromatin appears to be the principal target for its effects. In contrast, arsenic (III) is considered nongenotoxic but is able to target specific cellular proteins, principally through sulfhydryl interactions. Inhibition of transcription process by induces of heavy metal (Hg). Hg, Pb, Cd and As metal ions are damage DNA during replication process. Heavy metals Hg, Pb and Cd are reduce the process of protein synthesis.

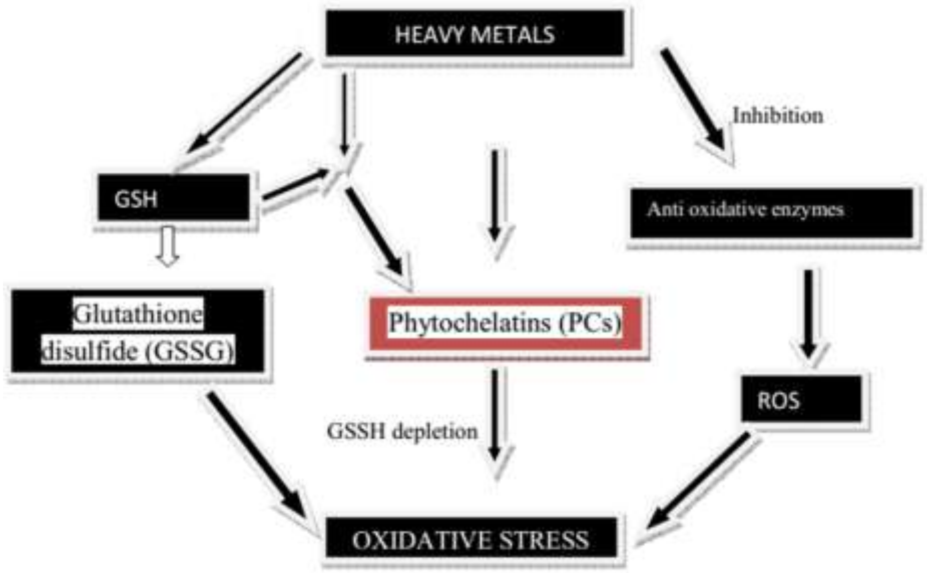

Fig. 1: Heavy metal induced oxidative stress and related cellular processes.

Scavenging of Reactive Oxygen Species

Heavy metals may enhance the generation of ROS (Reactive Oxygen Species) such as O2-, OH-, H2O2, and O2-. ROSs are regarded as the main source of damage to cells under the biotic and abiotic stresses [80-81]. ROSs are highly cytotoxic and can seriously react with vital biomolecules such as lipids, proteins, nucleic acid, these can cause lipid peroxidation, protein denaturation and DNA mutation [81,82]. Cu being a transitional element at higher concentration causes oxidative stress in cells by generating reactive oxygen species. Higher concentration of Cu can interrupt the electron flow during photosynthetic and respiratory processes and thus induces the generation of ROS. Cu can also induce the formation of highly reactive hydroxyl radical (OH-) from superoxide radical (O2-) or hydrogen peroxide (H2O2) via Habere Weiss reaction (Fig: 1). Cyanobacteria protective mechanism against heavy metal poisoning

Many techniques have been developed to remove the heavy metals from contaminated water, including: reverse osmosis, electrophoresis, ultra-ion exchange, chemical precipitation, phytoremediation, etc.

Detoxification of Heavy metals

Detoxification is the process of neutralizing or elimination of toxic metals in the environment. Heavy metals are severe environmental pollutants, and many of them are toxic even at very low concentrations. Detoxification is the process of neutralizing or elimination of toxins in the body. Heavy metal detoxification, is the removal of metallic toxic substances from the environment. Phytochelatins (PCs) and Metallothioneins (MTs) are different classes of heavy metal-binding protein molecules. Which are assumed to play an important role in the detoxification of Cd^{2+} and in the tolerance [83-84]. These are played a vital role in heavy metal (Cd^{2+}) detoxification process [85]. Torres et al., [86] demonstrated that algae *Cylindrothica fusiformis* produce carbohydrate as a defense mechanism against copper toxicity in stationary phase.

Metallothioneins (MTs)

Metallothioneins are thought to play an essential role in the intracellular regulation of the trace elements zinc and copper. MTs are gene-encoded polypeptides low molecular weight (6-7 kDa) and cysteine rich proteins divided into three different classes on the basis of cysteine content and structure.

Class 1: Polypeptides with locations of cysteine closely resembling those of equine renal MT, such as those isolated from Neurospora crass a and *Agaricus bisporus*.

Class II: Polypeptides with locations of cysteine only distantly related to those in equine renal MT, such as those isolated from Saccharomyces cerevisiae and *Synechococcus TX-20*.

Class III: Nontranslationary-synthesized metal-thiolate polypeptides isolated from higher plants, the fission yeast *Schizosaccharomyces pombe* and eukaryotic algae.

Phytochelatins (PCs)

Phytochelatins are enzymatically synthesized peptides, these are small glutathione-derived, enzymatically synthesized peptides, which bind metals and are principal part of the metal detoxification system in plants and algae [87-88]. PCs were isolated in 1988 from several "eukaryote" green algae exposed to heavy metal ions.

CONCLUSIONS

Cyanobacteria are predominantly aquatic organisms that must be able to discriminate between essential and non-essential heavy metal ions. In addition, they must maintain nontoxic concentrations of these ions inside their cells by phytochelatins.

REFERENCES

1. Pisciotta JM, Zou Y and Baskakov IV. 2010 Light-Dependent Electrogenic Activity of Cyanobacteria. *PLoS ONE*. 5(5)e10821:1-10
2. Marschner H. 1986 Mineral Nutrition in Higher Plants. London: Academic Press/Harcourt B & Company Publishers.
3. Adriano, D.C.1986. Elements in the Terrestrial Environment. Springer Verlag.
4. Modaihsh, A.S., Al-Swailem, M.S. and Mahjoub, M.O. 2004. Heavy metals content of commercial inorganic fertilizers used in the Kingdom of Saudi Arabia. Sultan Qaboos Univ. Agric. Marine Sci., 9(1): 21-25.
5. Chehregani, A., Malayeri, B.E., 2007. Removal heavy metals by native accumulator plants. International Journal of Agriculture and Biology 9, 462e465.
6. Wuana RA, Okieimen FE. 2011a. Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. ISRN Ecology 2011, 1-20.
7. Thangavel P, and Subbhuraam CV 2004 Phytoextraction: Role of hyper accumulators in metal contaminated soils. *P Indian Acad Sci B*.70:109–130.
8. Salem, HM., Eweida, EA. and Farag A 2000 Heavy metals in drinking water and their Environmental impact on human health. ICEHM, Cairo University, Egypt, September, 2000, page 542- 556.
9. Pulford, I.D. and Watson, C. 2003. Phytoremediation of heavy metal contaminated land by trees - A Review. *Environ. Int*., 29, 529–540.
10. Khan, M.S., A. Zaidi and P.A. and Wani. 2012a. Chromium plant growth promoting rhizobacteria interactions: Toxicity and management. In: Toxicity of Heavy Metals to Legumes and Bioremediation. (Eds.): A. Zaidi, P.A. Wani and M.S. Khan. Springer-Verlag Wien, pp. 67-88.
11. Khan MS, Zaidi A, Wani PA 2007 Role of phosphate-solubilizing microorganisms in sustainable agriculture-a Review. *Agron Sustain Dev*, 27:29-43.
12. Tariq, S.R., Shah, M.H., Shaheen, N., Khalique, A., Manzoor, S. and Jaffar, M. 2006 Multivariate analysis of trace metal levels in tannery effluents in relation to soil and water- A case study from Peshawar, Pakistan. Journal of Environmental Management, 79: 20-29.
13. Cervantes, C., J. Campos-Garcıa, S. Devars, F. Gutierrez-Corona, H. Loza-Tavera, J. C. Torres-Guzman, et al., 2001. Interactions of chromium with microorganisms and plants. *FEMS Microbiol. Rev*., 25: 335-347.
14. Panda, S.K., and S. Choudhury. 2005. Changes in nitrate reductase activity and oxidative stressresponse in the moss *Polytrichum commune* subjected to chro mium, copper and zincphytotoxicity. Brazilian Journal of Plant Physiology. 17: 191–7.
15. Ali, N. A., D. Dewez, O. Didur, and R. Popovic, 2006. Inhibition of photosystem II photochemistry by Cr is caused by alteration of both D1 protein and oxygen evolving complex. *Photosynth. Res*., 89: 81-87.
16. Meharg, A., 1994. Integrated tolerance mechanisms constitutive and adaptive plant responses to elevated metal concentrations in the environment. Plant.Cell Environ. 17, 989–993.
17. AyyaRaju, M Murthy. S.D.S.2011 Altered energy transfer in phycobilisomes of the cyanobacterium, under the influence of chromium (III) *Spirulina platensis*. Journal of Pure and Applied Sciences, 19:1-3.
18. Baryla A, Carrier P, Franck F, Coulomb C, Sahut C, Havaux M.2001. Leaf chlorosis in oilseed rape plants (Brassica napus) grown on cadmium-polluted soil: causes and consequences for photosynthesis and growth. *Planta* 212, 696–709.
19. Devi, SR, and Prasad MNV. Membrane lipid alterations in heavy metal exposed plants. In: Prasad MNV, Hagemeyer J, editors. Heavy metal stress in plants. From molecules to ecosystems. Berlin: Springer; 1999. pp. 99–116.
20. Janicka R, Katarzyna K, Marek B, Grazyna K 2008 Response of plasma membrane H+-ATPase to heavy metal stress in Cucumis sativus roots. Journal of Experimental Botany 59: 3721-3728. doi: 10.1093/jxb/ern219.
21. Mansour MMF, Salama KHA, Al-Mutawa MM 2003 Transport proteins and salt tolerance in plants. Plant Science 164: 891-900. doi: 10.1016/S0168-9452(03)00109-2.
22. Mansour MMF, Salama KHA 2004 Cellular basis of salinity tolerance in plants. Environmental and Exp Bot, 52: 113-122. doi: 10.1016/j.envexpbot.2004.01.009.
23. Sacina, M., Tobin, M. J. and Mullineaux, C. W. 2001 Diffusion of phycobilisomes on the thylakoid membranes on the cyanobacterium Synechococcus 7942; Effect of phycobilisome size, temperature and membrane lipid composition. *J. Biol.Chem*. 276, 46830-46834.

24. Venkataramanaiah, V. Murthy, S. D. S., and Sudhir, P. 2004 Effect of high temperature on photosynthetic electron transport activities of the cyanobacterium, Spirulina platensis. Photosynthetica 41, 331-334.
25. Wen, X., Gong, H. and Lu, C. 2005 Heat stress induces an inhibition of excitation energy transfer from phycobilisomes to Photosystem II but not Photosystem I in a cyanobacterium Spirulina maxima. Plant Physiol Biochem. 43, 389-395.
26. Sudhir, P., Pogoryelov, D., Kovacs, L., Garab, G. and Murthy, S.D. S. 2005 The effects of salt stress on photosynthetic electron transport and thylakoid membrane proteins in the cyanobacterium Spirulina platensis. *J. Biochem. Mol. Biol*. 38,481-485.
27. Li, H., Li, D., Yang, S., Xie, J. and Zhao, J. 2006 The state transition mechanism- simply depending on light on and off in Spirulina platensis. *Biochim. Biophys. Acta* 1757, 1512-1519.
28. Nagalakshmi, N. Prasad, M.N.V. 2001 Responses of glutathione cycle enzymes and glutathione metabolism to copper stress inScenedesmus bijugatus, *Plant Sci*.160:291e299.
29. Chanu,T.T, Panda, P. Mazumdar, P. Kumar, D. Sharma, G.D. Sahoo, L. Panda, S.K. 2012 Excess copper induced oxidative stress and response of antioxidants in rice, *Plant Physiol.Biochem*. 53:33e39.
30. Reddy, G.B., E. Ford and D. Aldridge, 1986. Seasonal changes in bacterial numbers and plant nutrients from point and non-point source ponds. Environ. Pollut., 40: 359-367.
31. Carpentier SC, Witters E, Laukens K, Van Onckelen H, Swennen R, Panis B: 2007 Banana **(***Musa spp.***)** as a model to study the meristem proteome: acclimation to osmotic stress. *Proteomics*, **7:**92-105.
32. Aspinall D, Paleg LG. 1981. Proline accumulation: physiological aspects. In: Paleg LG, Aspinall D, eds. The physiology andbiochemistry of drought resistance in plants.Australia: Academic Press, 205–240.
33. Ashraf M and Harris PJC. 2004. Potential biochemical indicators of salinity tolerance in plants. *Plant Science,* 166,3-16.
34. Naidu BP, Paleg LG, Aspinall D, Jennings AC, Jones GP. 1991. Amino acid and glycine-betaine accumulation in cold stressed seedlings. Phytochemistry 30, 407–409.
35. Schat H, Sharma SS, Vooijs R. 1997. Heavy metal-induced accumulation of free proline in a metal-tolerant and a non-tolerant ecotype of Silene vulgaris Physiologia Plantarum 101,477–482.
36. Watts, A., and J. J. H. H. M. DePont. 1985, 1986. Progress in Protein-Lipid Interactions, Vol. I, 1985; Vol. II, 1986. Elsevier, Amsterdam.
37. Sandmann G and Boger P 1980 Copper mediated lipid peroxidation processes in photosynthetic membranes. Plant Physiology 66: 797-800.
38. Gong P, Ogra, Y and Koizumi S 2000 Inhibitory effects of heavy metals on transcription factor Sp1. *Ind Health.* 38(2):224-227.
39. Zamble, D. B. 2008. Metalloregulatory Proteins. Wiley Encyclopedia of Chemical Biology. 1–10.
40. Masarovicova E, Cicak A, Stefanick I. 1999 Plant responses to air pollution and heavy metal stresses. In: Pessarakli M, ed. Handbook of Plant and Crop Stress. 2d ed. New York: Marcel Dekker,569–598.
41. Prasad MNV, Strzalka K 1999 Impact of heavy metals on photosynthesis. In Heavy Metal Stress in plants (Prasad MNV, Hagemeyer J eds.), 117-138, Springer Verlag, Berlin.
42. Zaccaro, M.C., Salazar, C., Zulpa de Caire, G., Storni de Cano, M., Stella, A.M., 2001. Lead toxicity in cyanobacterial porphyrin metabolism. Environ. Toxicol. 16, 61–67.
43. MacColl, R. (1998) Cyanobacterial phycobilisomes. J Struct Biol, 124 : 311–334.
44. Kana R, Prášil O, Mullineaux CW 2009 Immobility of phycobilins in the thylakoid lumen of a cryptophyte suggests that protein diffusion in the lumen is very restricted. FEBS Lett 583: 670–674. doi: 10.1016/j.febslet.2009.01.016.
45. Bertrand M, Poirier I. 2005. Photosynthetic organisms and excess of metals. Photosynthetica, 43: 345-353.
46. Kupper H, Setlik I, Setlikova E, Ferimazova N, Spiller M, Kupper FC 2003 Copper –induced inhibition of photosynthesis: Limiting steps of in vivo copper chlorophyll formation in Scenedesmus quadricauda. Functional Plant Biology 30:1187-1196.
47. Rai LC, Gau JP, Kumar HD.1981 Phycology and heavy-metal pollution. Biol. Rev. Cambridge Phil. Soc. 56: 99-151.
48. Wong PK, Chang L. 1991 Effects of copper, chromium and nickel on growth, photosynthesis, and chlorophyll a synthesis of Chlorella pyrenoidosa251. Environ. Pollut. 72: 127-140.
49. Corradi GM, Gorbi G, Rieci A, Torelli A, Bassi M. 1995 Chromium–induced sexual reproduction gives rise to a Cr tolerant progeny in Scenedesmus actus. Ecotoxicol. Environ. Safety 32: 12-19.
50. Genter RB. 1996 Ecotoxicology of inorganic stresses. In: RJ Stevenson, ML Bothwell, RL Lowe (eds.), Algal Ecology: Freshwater Benthic Ecosystems. Academic Press, San Diego, 403-468.
51. Conway HL 1978 Sorption of arsenic and cadmium and their effect on growth micronutrient utilization and photosynthesis pigment composite of Asterionella formosa.J. Fish Res Board. Can. 35: 286-294.
52. Rouillon, R, Piletsky, S.A, Breton, F., Piletska, E.V., Carpentier, R. In: Biotechnological Applications of Photosynthetic Proteins:Photosystem II Biosensors for Heavy Metals Monitoring Biochips, Biosensors and Biodevices Biotechnology Intelligence Unit 2006, pp 166-174.
53. Burda K, Kruk J, Strzalka K, Schmid GH. 2002 Stimulation of oxygen evolution in photosystem II by copper (II) ions. Z. Naturforsch.; 57c:853–857.
54. Yruela I, Alfonso M, de Zarate IO, Montoya G, Picorel R. 1993 Precise location of the Cu(II) inhibitory binding site in higher plant and bacterial photosynthetic reaction centers as probed by light-induced absorption changes. J. Biol. Chem. 268:1684–1689.
55. Yruela I, Alfonso M, Baron M, Picorel R. 2000 Copper effect on the protein composition of photosystem II. Physiol. Plant. 110:551–557.
56. Mohanty N, Vass I, Demeter S. 1989 Impairment of photosystem II activity at the level of secondary electron acceptor in chloroplasts treated with cobalt, nickel and zinc ions. Physiol. Plant. 76:386–390.
57. Andersson B, Styring S 1991 Photosystem II: molecular organization, function, and acclimation. Current Topic in Bioenergetics. 16: 1-81.
58. Dixit V, Pandey V, Shyam R. 2002 Chromium ions inactivate electron transport and enhance superoxide generation in vivo in pea (*Pisum sativum L.cv.Azad*) root mitochondria. Plant Cell Environ 25:687 -690.
59. Tripathi, R.D., Srivastava, S., Mishra, S. Singh, N. Tuli, R. Gupta, D.K. and Maathuis F.J.M. 2007, Arsenic hazards: Strategies for tolerance and remediation by plants. Trends Biotechnol. 25, 158 -1 65.
60. Belatik, A., Hotchandani, S., Tajmir-Riahi, H., Carpentier, R 2013 Alteration of the structure and function of photosystem I by Pb^{2+}. ournal of Photochemistry and Photobiology B: Biology 123:41-47.
61. Tuba Z and Csintalan Zs 1992 The effect of pollution on the physiological processes in plants. In: Kovács M, Podani J, Tuba Z, Turcsányi G, Csintalan Zs and Meenks JLD (eds) Biological Indicators in Environmental Protection, pp 169–191. Ellis Horwood, Chichester.
62. Robert I. Houtz, Ross O. 1988 Nable and george m. Cheniae Evidence for Effects on the in Vivo Activity of RibuloseBisphosphate Carboxylase/Oxygenase during Development of Mn Toxicity in Tobacco' Plant Physiol. 86, 1143-1149
63. Madhava Rao, K. V. and Sresty, T. V. 2000 Antioxidative parameters in the seedlings of pigeonpea (Cajanus cajan (L.) Millspaugh) in response to Zn and Ni stresses. Plant Sci., 157:113 – 128.
64. Léon, V., Rabier, J., Notonier, R., Barthelémy, R., Moreau, X., Bouraïma-Madjèbi, S., Viano, J. and Pineau, R. 2005 Effects of three nickel salts on germinating seeds of Grevillea exul var. rubiginosa, an endemic serpentine proteaceae. Annu. Bot., 95: 609–618.
65. De Filippis LF, Hampp R, Ziegler H. 1981 The effect of sub-lethal concentration of zinc, cadmium and mercury on EuglenaII. Respiration, photosynthesis and photochemical activities. Arch Microbiol. 128: 407-411.
66. Chaney RL 1993 Zinc phytotoxicity. In: Robson AD (ed) Zinc in soils and plants. Developments in plant and soil sciences. Kluwer Academic Publishers, Dordrecht, pp 135–150.

67. Van Assche F, Clijsters H 1986a Inhibition of photosynthesis by treatment ofPhaseolus vulgariswith toxic concentration of zinc: effects on electron transport and photophosphorylation. Physiol Plant 66:717–721.
68. Nash, S.M.B, Quayle, P.A., Schreiber, U. & Müller, F. 2005 The selection of a model microalgal species as biomaterial for a novel aquatic phytotoxicity assay. *Aquatic Toxicology*, **72**, 315–326.
69. Horcsik, Z. T., L. Kovacs, R. Laposi, 1. Meszaros, G. Lakatos et G. Garab. 2007. "Effect of chromium on photosystem 2 in the unicellular green alga, Chlorella pyrenoidosa". Photosynthetica, vol. 45, p. 65-69.
70. Devi, S.R. and Prasad MNV 2004 Membrane lipid alterations in heavy metal exposed plants, In: M.N.V. Prasad (2nd Ed), Heavy Metal Stress in plants: From biomolecules to ecosystems. Springer-Verlag. Heidelberg. Narosa New Delhi pp. 127-145.
71. Zsiros, O., Allakhverdiev, S.I., Higashi, S., Watanabe, M., Nishiyama, Y., Murata, N. 2006 Very strong UV-A light temporally separates the photoinhibition of photosystem II into light-induced inactivation and repair. – Biochim. biophys. Acta 1757: 123-129,.
72. Michel, K. P., and E. K. Pistorius. 2004. Adaptation of the photosynthetic electron transport chain in cyanobacteria to iron deficiency: the function of IdiA and IsiA. Physiol. Plant. 120:36–50.
73. Ivanov AG, Sane PV, Krol M, Gray GR, Balseris A, Savitch L.V, Öquist G, Hüner N.P.A. 2006 Acclimation to temperature and irradiance modulates PSII charge recombination. FEBS Letters, 580:2797-2802.
74. Bernal, M, Roncel, M, Ortega, JM, Picorel, R, Yruela I 2004. Copper effect on cytochrome b_{559} of photosynstem II under photoinhibitory conditions. *Physiol Plant*. 120:686-694.
75. Sujak, A. 2005. Interaction between cadmium, zinc and silver-substituted platocyanin and cytochrome b6f complex-heavy metals toxicity towards photosynthetic apparatus. Acta Physiologiae Plantarum 27(1):61-69.
76. Teige, M., B. Huchzermeyer. and G. 1990 Schulz Inhibition of chloroplast ATP synthasel ATPase is a primary effect of heavy metal toxicity in spinach plants. Biochem. Physioi. Pflanzen 186, 165-168.
77. Stobart A K,Griths W T, Ameen-Bukhari I, Sherwood R P,1985. The effect of Cd2+ on the biosynthesis of chlorophyll in leaves of barley. Plant Physiology, 63: 293–298.
78. Vajpayee P, Tripati RD, Rai UN, Ali MB, Singh SN 2000 Chromium accumulation reduces chlorophyll biosynthesis, nitrate reductase activity and protein content of *Nymphaea alba*. Chemosphere 41:1075-1082.
79. Hampp, R., K. Beulich and H. Zeigler. 1976. Effects of zinc and cadmium on photosynthetic CO2 fixation and Hill activity of isolated spinach chloroplasts Z. Pflanzenphysiol. 77:336-344.
80. Mittler, R., 2002, Oxidative stress, antioxidants and stress tolerance, Trends in Plant Science, 7, 405-410.
81. Vaidyanathan, H., P. Sivakumar, R. Chakrabarsty, G. Thomas, 2003, Scavenging of reactive oxygen species in NaCl-stressed rice (Oryza sativaL.)-differential response in salt-tolerant and sensitive varieties, Plant Science, 165, 1411-1418.
82. Quiles, M. J., N. I. López, 2004, Photoinhibition of photosystems I and II induced by exposure to high light intensity during oat plant grown effects on the chloroplastic NADH dehydrogenase complex, Plant Science,166, 815-823.
83. Grill, E., Zenk, M. H. 1985 Induction of heavy metalsequestering phytochelatin by cadmium in cell cultures of Rauwolfia serpentina. *Naturwissenschaften* 72, 432-433.
84. Grill,E., Winnacker, E.-L., Zenk, M. H. 1988 Occurence of heavy metal binding phytochelatins in plants growing in a mining refuse area. Experientia 44, 539 - 540.
85. Vatamaniuk OK, Bucher EA, Ward JT, Rea PA. 2001. A new pathway for heavy metal detoxification in animals phytochelatin synthase is required for cadmium tolerance in Caenorhabditis elegans. J. Biol. Chem. 276:20817–20.
86. Torres, M., J. Goldberg and T.E. Jensen, 1998. Heavy metal uptake by polyphosphate bodies in living and killed cells of *Plectonema boryanum* (Cyanophyceae). Microbios, 96: 141-147.
87. Cobbett C, Goldsbrough P. 2002 Phytochelatins and metallothioneins: roles in heavy metal detoxification and homeostasis. *Annu Rev Plant Biol* 53: 159–182.
88. Yurekli, F., Kucukbay, Z. 2003. Synthesis of phytochelatins in Helianthus annuus is enhanced by cadmium nitrate. In: Acta Bot. Croat. 62 (1), 21–25, 2003, ISSN 0365–0588.