Toxicological Impact of Herbicides on Cyanobacteria

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

The use of herbicides in modern agriculture to eradicate weeds has led to serious environmental contamination resulting in a loss of growth and development of many beneficial micro-organisms. Low cost, easy availability, lax in regulatory mechanism have contributed to the continuous use of the herbicides in tropical and subtropical regions. The removal of these herbicides from soil and aquatic systems is a difficult task and as a result herbicides persist in these ecosystems for a long period of time. Cyanobacteria are a diverse group of gram-negative photosynthetic prokaryotes. Their life processes require only water, carbon dioxide, inorganic substances and light and these organisms contribute greatly to terrestrial as well as aquatic ecosystems through their ability to increase soil fertility by adding nitrogen, enhancing water holding capacity, releasing vitamins and plant stimulating hormones, adding extra cellular polysaccharides and by solubilizing phosphates.

The present paper review responses of cyanobacteria to herbicides and impact of herbicides on photosynthetic pigments, photosynthesis and nitrogen assimilation by cyanobacteria. The tolerance mechanisms and herbicide biodegradation potential of cyanobacteria are also reviewed.
Keywords: Cyanobacteria; herbicide; photosynthesis; respiration; antioxidant system; biodegradation.

1. INTRODUCTION

Feeding of over nine billion people expected to inhabit our planet by 2050 will be an unprecedented challenge for all human beings [1]. The production of enough food for the human population across the globe in 2050 will be possible but at an unacceptable cost. In view of the world’s limited croplands and growing population [2], it is necessary to take all measures to increase crop production in order to ensure food safety [3]. This will largely depend upon the agro-research from high quality seeds to low cost farming practices [4]. More than 8,000 species of weeds, 9,000 species of insects and pests and 50,000 species of plant pathogens damage agricultural crops across the globe. To this loss, weeds account for 13% loss. Insect pests and plant pathogens cause an estimated loss of 14% and 13%, respectively [5]. It has been estimated that without pesticide application, the loss of cereals, vegetables and fruits from pest injury would reach 32, 54 and 78%, respectively [6]. Crop loss from pests declines by 35% from 42% when pesticides are used. Thus, the use of pesticides is indispensable in agricultural production system. Presently, about one-third of the agricultural products are produced by using pesticides [7].

Agriculture plays a major role in the Indian economy as more than 70% of India’s population is directly dependent on it and 27% of country’s gross domestic product stems from it. After many years of struggle with food shortages, India has made good strides in food production from 51 million tonnes in 1950-51 to 212 million tonnes in 2001-02. This is due to introduction of new crop varieties and improved farming practices [4]. Thus, microbial communities in freshwater ecosystems including agri-ecosystem are directly or indirectly affected by these compounds. For example, many commercial herbicides act by binding to Photosystem II (PS-II), which is a pigment-protein membrane complex [11]. PS-II inhibitors have a direct impact on photosynthetic aquatic microorganisms that contain the same PS-II apparatus as the terrestrial weeds targeted by these herbicides. Beside this direct impact on photosynthetic microorganisms, herbicides can also have an indirect impact on non-photosynthetic species that are not susceptible to PS-II inhibitors. These effects on microbial communities can have a critical impact on the overall functioning of freshwater ecosystems. Indeed, microorganisms including cyanobacteria contribute to most of the primary production in these systems [12]. The microorganisms are also involved in nutrient cycling and decomposition [13]. Depending on the kind of ecosystem, both these communities must be considered when attempting to evaluate the impact of herbicides on microbial communities.

Cyanobacteria are morphologically, physiologically and developmentally most diverse group of photosynthetic prokaryotes with low level of cellular differentiation that constitute one of the major eubacteria phyla [14,15]. They also share characteristics of both gram-negative bacteria and photosynthetic eukaryotes. These organisms have existed 2.5 billion years ago in the earth’s geological history as evidenced by the microfossils, detected from early, middle and late Precambrian strata. They seem to have played the most important role in preparing the earth for the evolution of higher life forms by contributing to significant increase in oxygen level [16]. These microorganisms exhibit relatively simple morphology and show maximum three cell types: vegetative cells, heterocysts and akinetes. Heterocyst differentiation occurs under nitrogen starvation. Structurally and functionally, the heterocysts are the ideal sites for nitrogen fixation [17].
Classical taxonomists have classified cyanobacteria into five orders i.e., Chroococcales, Chamaesiphonales, Pleurocapsales, Nostocales and Stigonematales [18,19]. On the basis of number of morphological, physiological and genetic traits, Rippka et al. [20] have taxonomically revised this group and recognized five sections. Section I comprises Chroococcales and Chamaesiphonales which reproduce by binary fission in one, two or three planes or by budding. Section II includes members of Pleurocapsales which reproduce by baeocytes (endospores or exospores) which are formed by multiple fission. Section III comprises non-heterocystous filamentous oscillatorian members. Section IV and V correspond to Nostocales and Stigonematales, respectively, of Desikachary [19]. Following Rippka et al. [20] new classification has been proposed which recognizes Chroococcales, Pleurocapsales, Oscillatoriales, Nostocales and Stigonematales as the five orders of cyanobacteria [21]. Nucelic acid sequencing of cyanobacteria is the beginning to elucidate the evolutionary relationships among cyanobacteria. Recently, Lee [22] suggested three orders of cyanobacteria i.e. Chroococcales (unicellular cyanobacteria), Oscillatoriales (filamentous cyanobacteria) and Nostocales (filamentous cyanobacteria with heterocysts).

Cyanobacteria are ubiquitous in their distribution and grow in all sorts of aquatic and terrestrial environments. They survive in a wide variety of extreme environmental conditions when they are exposed to various types of natural stresses, such as nutrient limitation, pesticides, pollution, drought, salinity, temperature, pH, light intensity and quality, etc. [23]. Illustrating their capacity to acclimate to extreme environments, a protein in the cyanobacterial thylakoid membranes was identified as a sensitive protein to environmental stresses such as drought, nutrition deficiency, heat and chemical stress [24]. Many cyanobacterial species are capable of not only surviving, but thriving in conditions previously thought to be inhabitable.

Cyanobacteria perform biologically two important key activities carbon fixation and nitrogen fixation and enrich the soil with humus and nitrogen content, improve water holding capacity, release vitamins, plant stimulating hormones, extra cellular polysaccharides and also solubilize phosphates [21,25-27]. It has been reported that more than half of the total nitrogen used by paddy crop derives from the native soil nitrogen pool which is maintained through biological nitrogen fixation by both hetero- and autotrophs in soil [28]. Non-heterocystous forms of cyanobacteria which predominantly occur in rice fields may also fix atmospheric nitrogen under anaerobic conditions [29]. *Plectonema* [30], *Trichodesmium* [31], *Phormidium*, *Lyngbya*, *Chlorogloea*, *Gloeocapsa* and *Synechocystis* [32] have been reported to fix atmospheric nitrogen. The characteristics of cyanobacteria to fix carbon as well as nitrogen fixation have made them an important component of both aquatic as well as terrestrial ecosystems. These microorganisms are applied in rice fields as biofertilizer for better crops yield [33].

Soil nitrogen is the main source of nitrogen for crop growth and rice crop consumes 50% N from soil [25]. Nitrogen-fixing cyanobacteria are abundantly present in the rice field and are important microbes for the maintenance of rice field fertility through carbon and nitrogen fixation [26]. The use of cyanobacterial biofertilizer is considered to be a good management of paddy fields since their use not only increases fertility of the soil but is also eco-friendly. Thorough investigations on deleterious effects of pesticides including herbicides on cyanobacteria are required since utilization of cyanobacterial biofertilizer in paddy fields requires that strains be tolerant to a variety of routinely used agrochemicals.

The effects of pesticides on algae have been extensively reviewed from time to time [34-38]. The literature surveyed by the authors revealed that impact of more than fifty five herbicides on cyanobacteria in one or another way has been studied. As per the classification given by Mallory-Smith and Retzinger [39], these herbicides belong to 15 groups according to their mode of action on target plants (Table 1). The parameters studied include growth, tolerance limit, photosynthetic pigments, carbon assimilation, defence mechanism, nitrogen assimilation and biodegradation. In this review current status of impact of herbicides on cyanobacteria is discussed.

### 2. GROWTH INHIBITION AND TOXICITY

Cyanobacteria are quite sensitive to herbicides, because they share many of the physiological features of higher plants. Differences have been observed between the tolerance to herbicides by cyanobacteria and other organisms. The different algal species exhibit different sensitivity to
different herbicides depending on the species tested, concentration and nature of herbicide used [27,40-43]. For example, it has been observed that hexahydropyridine was more toxic to green algae, diatoms and duckweed than to cyanobacteria, whereas green algae were more tolerant to diquat than cyanobacteria and diatoms [44]. The chronic exposure of hexahydropyridine to cyanobacterial dominant phytoplankton community of a forest lake at 1.0 ppm resulted in reduction of biomass of all dominant phytoplankton groups including cyanobacteria [45]. Ahluwalia et al. [46] proved that the incorporation of relatively higher doses (>5 ppm) of diquat into the culture of Allomonas variabilis and Anabaena inaequalis at EC50 values ranging between1.0 and 8.5 ppm for both growth criteria. In contrast, de-isopropyl atrazine was toxic towards A. variabilis and A. inaequalis with EC50 ranging from 2.5 to 9.2 ppm for both criteria. Both diamino and hydroxyl-paraquat were less toxic to cultures tested yielding EC50 less than 10 ppm [54]. De-Loranzo et al. [38] obtained EC50 value of atrazine at 0.47 ppm for cyanobacterium Anabaena flosaquae. Another study revealed that atrazine at 88 ppb significantly reduced the growth of unicellular cyanobacterium Synechocystis sp. [55]. Low dose of atrazine (10 ppb) did not affect the growth and cell volume of Arthospira and Synechocystis while more than 100 ppb atrazine inhibited growth [53].

Wild type and multiple herbicide resistant (MHR) stain of Anabaena variabilis tolerated pure and formulated form of atrazine up to 4 and 1 ppm, respectively, indicating formulated form of atrazine was more toxic than pure form [56]. Atrazine at 4.2 ppm caused 50% decrease in growth of Microcystis novacekii demonstrating the potential of the organism to tolerate high concentrations of this herbicide in fresh water environments [57]. Ten species of phytoplankton belonging to green algae, diatoms and cyanobacteria were exposed to atrazine for 72 h at EC50 concentrations and light of different intensities to compare their combined effect. The data revealed that cyanobacteria were less tolerant to atrazine than green algae and diatoms [58].

Cyanobacteria Synechocystis PCC 6803 and Anabaena variabilis ATCC 29413 showed high degree of tolerance to glyphosate and its various formulations. Significant differences in growth were observed at 10 mM glyphosate. The decreasing order of toxicity of these formulations were as RoundupR> isopropylamine salt > free acid [59]. Other cyanobacteria such as Anabaena sp., Arthospira fusiformis, Leptolyngbya boryana, Microcystis aeruginosa, Nostoc punctiforme and Spirulina platensis tolerated glyphosate in the range of 1-10 mM [60]. Growth of wild-type and glyphosate-sensitive (Gs) cells of Microcystis aeruginosa was inhibited when they were cultured with 120
ppm glyphosate but after further incubation for several weeks, occasionally the growth of rare cells resistant (Gr) to the herbicide was found [61]. The effect of glyphosate (37-150 ppm) on the growth of *Merismopedia glauca* was dose dependent with maximum growth rate and generation time being 1.5 d^{-1} and 0.44 d^{-1}, respectively [62]. The application of commercial formulation of glyphosate roundup (6 and 12 ppm) on fresh water microbial communities in artificial earthen mesocosms significantly increased the population of cyanobacteria by 4.5 folds in periphytic assemblages [63]. Vera et al. [64] have shown that diatoms were more susceptible than cyanobacteria to glyphosate. In a study on ecological risks assessment of organophosphorus pesticides on bloom forming cyanobacterium *Microcystis wesenbergii*, it was observed that isopropyl ammonium salt of glyphosate (6.84 μM L^{-1}) showed medium growth inhibitory effect [65].

Nitrogen-fixing cyanobacteria were relatively tolerant to 2,4 D compared to non-nitrogen fixing ones under field conditions. Low concentration (1 mM) of 2,4 D and 2-methyl-4-chlorophenoxyacetic acid (MCPA) did not affect the growth of *Anabaena UAM 202, UAM204 and Nostoc UAM205* while higher dose (10 mM) was inhibitory when growth was measured in terms of dry weight biomass [66]. The growth of *Gloeocapsa* was not affected significantly at 100-150 ppm while 175-200 ppm of 2,4 D inhibited growth by 50-75% after 8 days of incubation [67]. Tiwari et al. [68] compared the tolerance level of 28 non-heterocystous filamentous cyanobacteria isolated from rice fields using Chl a as growth parameter. The range of tolerance of cyanobacteria to 2,4 D was 25 to 200 ppm with *Lyngbya spiralis* being the most tolerant (200 ppm). Tripathi et al. [69] revealed that 2,4 D above 600 μM was inhibitory to *Nostoc muscorum* and *Synechococcus PCC 7942*. In a nine day exposure experiment, 50 percent survival of cyanobacterial isolates belonging to genera *Chroococcus, Microcystis* and *Synechocystis* was observed in 6.84 μM L^{-1} of 2,4 D [70].

Herbicide 3-(3,4-dichlorphenyl)-1,1 dimethyl urea (DCMU) along with fluometuron, atrazine, ametryn inhibited the growth of *Plectonema boryanum* [71]. DCMU (0.2 ppm) inhibited the growth of diazotroph *Nostoc muscorum* [72]. The cyanobacterial strain SG2 of *Nostoc* tolerated DCMU up to 15 ppm [73]. *Synechococcus PCC 7042, Nostoc* and *Spirulina platensis* exhibited 80% inhibition in growth by 20 μM DCMU after 48 hr of treatment [69]. DCMU (0.5 ppm) was found to be more toxic as compared to atrazine (0.6 ppm) to both parent and mutant strain of *Anabaena variabilis* [56]. Leunert et al. [74] compared the sensitivity of cyanobacteria and green algae to DCMU using delayed fluorescence decay kinetics. It was found that cyanobacteria were more sensitive to DCMU than green algae.

Monsulfuron at low concentration (0.03-0.3 nmol L^{-1}) stimulated growth of *Anabaena flosaquae, Anabaena azollae* and *Anabaena azotica* while higher concentrations (3-300 nmol L^{-1}) were inhibitory. The most sensitive species was *A. flosaquae* followed by *A. azollae* and *A. azotica* [75]. Studies also revealed that the growth of *A. flosaquae* decreased significantly when exposed to monosulfuron (0.008-800 ppm) under 2000, 3000 and 4000 lux light intensity. The cell number and growth rate were reduced with most sensitive light intensity being 4000 lux followed by 3000 lux and 2000 lux [76]. The supplementation of nitrogen further decreased the growth of *Anabaena flosaquae* in presence of monosulfuron (0.016-0.3 ppm) indicating synergistic effect of herbicide and nitrogen [77].

Butachlor exhibited moderate to high toxicity to cyanobacteria. The growth of *Anacystis nidulans, Nostoc muscorum* and *Anabaena dolioolum* was completely inhibited at 2.5, 5 and 20 ppm, respectively, of butachlor [78]. Butachlor at 6-8 ppm was lethal to *Nostoc linckia, Nostoc calicola, Nostoc* sp., and *A. dolioolum* [79]. Butachlor exhibited low toxicity to *Nostoc* sp., *N. punctiforme, Nostoc calicola, Anabaena variabilis, Gloeocapsa* sp., *Aphanocapsa* sp. and *Aulosira fertilissima* with EC_{50} values between 9.7 and 15 ppm [80 and 81]. In toxicity studies, Ge–Xian–Mi (*Nostoc*) had 96 h EC_{50} value of 169 μM butachlor [82]. *Aulosira fertilissima* had 16 d EC_{50} value equivalent to 65 μM [83]. He et al. [84] observed that butachlor above 120 ppm was lethal to *Nostoc* sp. Another study revealed that *Nostoc muscorum* tolerated butachlor upto 20 ppm [85]. Butachlor (25-36 μM) caused 50% decrease in growth of *Anabaena* 7120, *Anabaena dolioolum* and *Anabaena LC31* [86].
Table 1. Summary list of toxicity tests parameters of herbicides to cyanobacteria

| Sr. no. | Herbicide | Chemical name | Chemical family | Organism(s) | Parameter(s) studied | Reference |
|---------|-----------|---------------|-----------------|-------------|---------------------|-----------|
| A       | Clodinafop-propargyl | prop-2-ynyl (R)-2-(4-(5-chloro-3-fluoro-2-pyridyloxy) phenoxy) propionate | Aryloxyphenoxy-propionate | Nostoc muscorum | Toxicity | Singh et al. [102] |
| 2       | Cyhalofop butachlor | (R)-2-(4-(4-cyano-2-luorophenoxy) phenoxy)propanoic acid | Aryloxyphenoxy-propionate | Nostoc muscorum | Toxicity | Singh et al. [102] |
| 3       | Diclofop | (RS)-2-(4-(2,4-dichlorophenoxy) phenoxy)propionic acid | Aryloxyphenoxy-propionate | Anabaena flos-aquae, Microcystis flosaquae and Microcystis aeruginosa | Toxicity | Ma et al. [40] |
|         |           |               |                 | Microcystis aeruginosa | Growth, protein, ultra cell structure | Ye et al. [98] |
|         |           |               |                 | Microcystis aeruginosa | Oxidative stress | Ye et al. [152] |
| B       | Fenoxaprop-p-ethyl | ethyl (R)-2-(4-(6-chloro-1,3-benzoazol-2-yloxy) phenoxy) propionate | Aryloxyphenoxy-propionate | Anabaena sp., Nostoc commune and Anabaena variabilis | Growth, photosynthesis and nitrogen fixation | Okmen et al. [116] |
|         |           |               |                 | Anabaena, Nostoc and Nodularia | Photosynthetic pigments and photosynthesis | Chen et al. [82] |
|         |           |               |                 | Nostoc spongiforme | Growth and nitrogen fixation | Okmen et al. [88] |
|         |           |               |                 | Anabaena sp., Cylindrospermum raciborsckii, Microcystis aeruginosa and Pseudanabaena limnetica | Growth rate | Spencer et al. [89] |
|         |           |               |                 | Anabaena sp., Gloeothecae sp., and Synechocystis sp. | Toxicity | Netherland et al. [116] |
|         |           |               |                 | Nostoc commun | photosynthetic pigments and photosynthesis | Okmen and Ugur. [145] |
| 2       | Chlorosulfuron | 1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea | Sulfonylurea | 20 fresh water microalgae including cyanobacteria | Growth Inhibition | Nyström et al. [51] |
| 8       | Metasulfuron (Methyl metsulfuron) | 2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfonyl) benzoic acid | Sulfonylurea | 20 fresh water microalgae including cyanobacteria | Growth inhibition | Sabater and Carrasco [52] |

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| Sr. no. | Herbicide            | Chemical name                        | Chemical family                     | Organism(s)                          | Parameter(s) studied                                      | Reference                                      |
|--------|----------------------|--------------------------------------|-------------------------------------|--------------------------------------|----------------------------------------------------------|------------------------------------------------|
| 9      | Monosulfuron         | 2-((4-methylpyrimidin-2-yl)carbamoylsulfamoyl) benzoic acid | Pyrimidinylsulfonil-urea            | Nostoc muscorum, Anabaena flosaquae, Anabaena azolae and Anabaena azotica | Toxicity, Growth, acetolactate synthetase activity and amino acids | Singh et al. [102], Shen et al. [75] |
|        |                      |                                      |                                     | Anabaena flosaquae                    | Growth and photosynthetic pigments                        | Shen et al. [76 and 77]                       |
|        |                      |                                      |                                     | Anabaena flosaquae, Anabaena azolae and Anabaena azotica | Growth, photosynthesis and nitrogenase activity           | Shen et al. [133]                            |
| 10     | Sulfosulfuron        | 1-(4,6-dimethoxypyrimidin-2-yl)-3-(2-ethylsulfonylimidazo(1,2-a)pyridin-3-ylsulfonil) azura | Pyrimidinylsulfonil-urea            | Nostoc muscorum, Anabaena flosaquae, Anabaena azolae and Anabaena azotica | Toxicity                                               | Singh et al. [102]                            |
| 11     | Imazamox             | 2-[[RS]-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-5-methoxymethyl nicotinic acid | Imidazolinone                       | Anabaena sp., Cylindrospermum raciborsckii, Microcystis aeruginosa and Pseudanabaena limnetica | Toxicity                                               | Netherland et al. [116]                      |
| 12     | Penasulam            | 3-(2,2-difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-α,α,α-trifluorotoluene-2-sulfonamid | Triazolopyrimidine sulphonamide     | Anabaena sp., Cylindrospermum raciborsckii, Microcystis aeruginosa and Pseudanabaena limnetica | Toxicity                                               | Netherland et al. [116]                      |
|        |                      |                                      |                                     |                                     |                                                          |                                                |
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|        |                      |                                      |                                     |                                     |                                                          |                                                |
| C      | Inhibitors of microtubule assembly |                           |                                     |                                     |                                                          |                                                |
| 13     | Pendimethalin        | N-(1-ethylpropyl)-2,6-dinitro-3,4-xyldine | Dinitroaniline                      | Nostoc muscorum                      | Toxicity                                               | Singh et al. [102]                            |
| 14     | Trifluralin          | α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine | Dinitroaniline                      | Plectonema boryanum and Cyanophage LPP-1 | Growth Inhibition                                       | Mallison and Cannon [71], Aslim and Ozturk [70], Koksoy and Aslim [114] |
|        |                      |                                      |                                     | Chroococcus sp., Microcystis sp. and Synechococcus sp. | Toxicity                                               |                                                |
|        |                      |                                      |                                     | Microcystis sp., Synechocystis sp., Chroococcus sp. and Synechococcus sp. | Growth                                               |                                                |
| D      | Synthetic auxin      |                                     |                                     |                                     |                                                          |                                                |
| 15     | 2,4 D                | (2,4, dichlorophenoxy) acetic acid    | Phenoxy acids                       | Anabaena                           | Nitrogen fixation and ammonia excretion                | Subramanian and Shanmugasundaram [139], Leganés and Fernández-Valiente [66], Tözüm-Calgan and Sivaci-Gün [67], Tiwari et al. [68] |
|        |                      |                                      |                                     | Anabaena, Nostoc and Nodularia      | Growth, photosynthesis and nitrogen fixation            |                                                |
|        |                      |                                      |                                     | Gloeocapsa                         | Growth and nitrogen fixation                           |                                                |
|        |                      |                                      |                                     | Pseudanabaena, Limnotrix            | Dry weight and generation times                         |                                                |
| Sr. no. | Herbicide | Chemical name | Chemical family | Organism(s) | Parameter(s) studied | Reference |
|--------|-----------|---------------|-----------------|-------------|----------------------|-----------|
| 1      | Phormidium, Microcoleus, Plectonema, Lyngbya and Oscillatoria | Synechococcus PCC7942, Nostoc muscorum and Spirulina platensis | Hypersaline cyanobacterial mat | Nostoc muscorum, N. punctiforme, N. calcicola, Anabaena variabilis, Gloeocapsa sp. and Aphanocapsa sp. | Growth and photosynthesis | Tripathi et. al. [69] |
| 2      |  | Oscillatoria sp. | | Oscillatoria sp. dominated cyanobacterial mat | Biodegradation | Singh and Datta [91 and 81] |
| 3      |  | Chroococcus sp., Microcystis sp. and Synechococcus sp. | | Anabaena fertilissima, Aulosira fertilissima and Westiellopsis prolifica | Sorption | Singh et al. [90] |
| 4      | Anabaena fertilissima | | | | Toxicity | Kumar et. al. [177] |
| 5      | Nostoc muscorum | | | | Photosynthetic pigments, carbohydrates, amino acids, protein, phenol, NR, GS and SDH activity | Singh et al. [102] |
| 6      | Anabaena variabilis | | | | Toxicity | Singh et al. [27] |
| 7      |  | Microcystis sp., Synechocystis sp., Chroococcus sp. and Synechococcus | | Anabaena fertilissima, Aulosira fertilissima and Westiellopsis prolifica | Photosynthetic pigments, photosynthesis, respiration, nitrogen fixation and GS activity | Koksoy and Aslim [114] |
| 8      |  | Anabaena fertilissima, Aulosira fertilissima and Westiellopsis prolifica | | Anabaena torulosa | Biodegradation | Kumar et al. [172] |
| 9      |  | Synechococcus aeruginosus | | | Biosensor | Shing et al. [178] |

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| Sr. no. | Herbicide | Chemical name | Chemical family | Organism(s) | Parameter(s) studied | Reference |
|---------|-----------|---------------|-----------------|-------------|---------------------|-----------|
| 16      | Methylchloro phenoxy acetic acid (MCPA) | (4-chloro-3-methylphenoxy)acetic acid | Phenoxy acids | Anabaena, Nostoc and Nodularia | Growth, photosynthesis and nitrogenase activity | Leganés and Fernández-Valiente [66] |
|         |           |               |                 | Anabaena sp. and Microcystis viridis | Photosynthesis, antioxidant enzymes and DNA damage | Chen et al. [125] |
| 17      | Triclopyr | 3,5,6-trichloro-2-pyridyloxyacetic acid | Quinolone carboxylic acid | Anabaena flosaquae, Microcystis flosaquae and Microcystis aeruginosa | ToxiCity | Ma et al. [40] |

**E Inhibitors of photosynthesis at PS-II site A**

| Sr. no. | Herbicide | Chemical name | Chemical family | Organism(s) | Parameter(s) studied | Reference |
|---------|-----------|---------------|-----------------|-------------|---------------------|-----------|
| 18      | Ametryn   | N\(^2\)-ethyl-N\(^4\)-isopropyl-6-methylthio-1,3,5-triazine-2,4-diamine | Triazine | Plectonema boryanum and Cyanophage LPP-1 | Growth Inhibition | Mallison and Cannon [71] |
|         |           |               |                 | Anabaena flosaquae, Microcystis flosaquae and Microcystis aeruginosa | Toxicity | Ma et al. [40] |
| 19      | Atrazine  | 6-chloro-N\(^2\)-ethyl-N\(^4\)-isopropyl-1,3,5-triazine-2,4-diamine | Triazine | Anabaena flosaquae and Selenastrum capricornutum | Growth Inhibition | Mallison and Cannon [71] |
|         |           |               |                 | Anabaena inaequalis, Aphanizomenon flos-aquae, Pseudoanaabaena sp., Oscillatoria sp., Microcystis aeruginosa, Cyclotella meneghiana, Nitzschia sp., Scenedesmus quadricauda, Selenastrum capricornutum and Vibrio fischeri | Growth | Abou-Waly et al. [180] |
|         |           |               |                 | Synechococcus sp. | 7-day carbon uptake | Peterson et al. [50] |
|         |           |               |                 | Synechocystis sp. strain PCC 6893 | Biosensor | Preuss and Hall [181] |
|         |           |               |                 | Cyanobacterial strain SG2 | Resistance | Narusaka et al. [127] |
|         |           |               |                 | Synechocystis sp. strain PCC 6803 | psbA1 gene | Sajjaphan et al. [73] |
|         |           |               |                 | Synechococcus sp., Arthospira sp., Ankistrodesmus falcatus, Chlorella vulgaris, Staurastrum cristatum, Cyclotella meneghiana, Nitzschia palea, Cryptomonas ovata and Euglena gracilis | Biosensor | Shao et al. [179] |
|         |           |               |                 | Synechococcus elongates | Growth Inhibition | Lockert et al. [53] |
|         |           |               |                 | Synechococcus elongates and Chlorella vulgaris | Biosensor | Kobilžek et al. [182] |
|         |           |               |                 | | Herbicide removal | González-Barreiro et al. [173] |
| Sr. no. | Herbicide   | Chemical name | Chemical family | Organism(s)                                                                 | Parameter(s) studied                              | Reference |
|--------|-------------|---------------|-----------------|----------------------------------------------------------------------------|---------------------------------------------------|-----------|
| 20     | Bromacil    | (RS)-5-bromo-3-sec-butyl-6-methyluracil | Uracil          | Microbial assemblages, *Thermosyneochococcus elongatus*, *Synecochoccus sp.*, *Pseudokirchneriella subcapitata*, *Isochrysis galbana*, *Dunaliella tertiolecta* and *Pseudodactylum tricornutum*, *Anabaena variabilis* | Chlorophyll a, Carbon assimilation and biomass, Photosystem-II | Downing et al. [183] |
|        |             |               |                 | *Anabaena variabilis*, *Nostoc muscorum*, *Microcystis novacekii* | Low molecular weight molecules, lipids, polysaccharides and proteins | Zimmermann et al. [184] |
|        |             |               |                 | *Anabaena inaequalis, Aphanizomenon flosaquae, Pseudoanabaena sp., Oscillatoria sp., Microcystis aeruginosa, Cyclotella meneghiana, Nitzschia sp., Scenedesmus quadricauda, Selenastrum capricornutum* and *Vibrio fisheri* | Photosynthetic pigments and photosynthesis | Weiner et. al. [55] |
| 21     | Cyanzine    | 2-(4-chloro-6-ethylamino-1,3,5-triazin-2-ylamino)-2-methylpropiononitrile | Triazine        | Anabaena inaequalis, Aphanizomenon flosaquae, Pseudoanabaena sp., Oscillatoria sp., Microcystis aeruginosa, Cyclotella meneghiana, Nitzschia sp., Scenedesmus quadricauda, Selenastrum capricornutum* and *Vibrio fisheri* | Chlorophyll a, photosynthesis, respiration and heterocyst frequency | Singh et al. [56] |
|        |             |               |                 | Anabaena inaequalis, Aphanizomenon flosaquae, Pseudoanabaena sp., Oscillatoria sp., Microcystis aeruginosa, Cyclotella meneghiana, Nitzschia sp., Scenedesmus quadricauda, Selenastrum capricornutum* and *Vibrio fisheri* | Toxicity | Singh et al. [56] |
|        |             |               |                 | *Anabaena flosaquae, Microcystis flosaquae* and *Microcystis aeruginosa* | Bioaccumulation removal | Campos et al. [57] |
|        |             |               |                 | *Anabaena inaequalis, Aphanizomenon flosaquae, Pseudoanabaena sp., Oscillatoria sp., Microcystis aeruginosa, Cyclotella meneghiana, Nitzschia sp., Scenedesmus quadricauda, Selenastrum capricornutum* and *Vibrio fisheri* | Toxicity and photosynthesis, 7-day carbon uptake | Debiol et al. [58] |
| 22     | Hexazinone  | 3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione | Triazine        | Anabaena flosaquae, Microcystis flosaquae and *Microcystis aeruginosa* | Toxicity | Ma et al. [40] |
|        |             |               |                 | *Anabaena flosaquae and Selenastrum capricornutum* | Growth | Abou-Waly et al. [180] |
| Sr. no. | Herbicide | Chemical name | Chemical family | Organism(s) | Parameter(s) studied | Reference |
|---------|-----------|---------------|----------------|-------------|----------------------|-----------|
| 23      | Metribuzin | 4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one | Triazinone      | Anabaena inaequalis, Aphanizomenon flos-aquae, Pseudoanabaena sp., Oscillatoria sp., Microcystis aeruginosa, Cyclotella meneghiana, Nitzschia sp., Scenedesmus quadricauda, Selenastrum capricornutum and Vibrio fisheri | 7-day carbon uptake | Peterson et al. [44 and 50] |
| 24      | Prometryne | N²,N⁴-diisopropyl-6-methylthio-1,3,5-triazine-2,4-diamine | Triazinone      | Anabaena inaequalis, Aphanizomenon flos-aquae, Pseudoanabaena sp., Oscillatoria sp., Microcystis aeruginosa, Cyclotella meneghiana, Nitzschia sp., Scenedesmus quadricauda, Selenastrum capricornutum and Vibrio fisheri | Toxicity | Singh et al. [102] |
|         |           |               |                | Nostoc muscorum Anabaena sp. | Photosynthetic pigments Growth and photosynthetic pigments Toxicity | Okmen et al. [120] Shen et al. [185] |
| 25      | Simazine  | 6-chloro-N²,N⁴-diethyl-1,3,5-triazine-2,4-diamine | Triazinone      | Anabaena inaequalis, Aphanizomenon flos-aquae, Pseudoanabaena sp., Oscillatoria sp., Microcystis aeruginosa, Cyclotella meneghiana, Nitzschia sp., Scenedesmus quadricauda, Selenastrum capricornutum and Vibrio fisheri | 7-day carbon uptake | Peterson et al. [50] |
|         |           |               |                | Synechococcus elongatus | Biosensor | Kobilžek et al. [182 and 186] |
|         |           |               |                | Anabaena flosaquae, Microcystis flosaquae and Microcystis aeruginosa Synechocystis sp. strain PCC 6803 | Toxicity | Ma et al. [40] |
| 26      | Simetryn  | N²,N⁴-diethyl-6-methylthio-1,3,5-triazine-2,4-diamine | Triazinone      | Anabaena flos-aquae, Microcystis flos-aquae and Microcystis aeruginosa | Biosensor | Shao et al. [179] |
|         |           |               |                | Thermosyneochococcus elongatus and Chlorella vulgaris | Toxicity | Ma et al. [40] |
| 27      | Terbutryn | N⁴-tert-butyl-N⁴-ethyl-6-methylthio-1,3,5-triazine-2,4-diamine | Triazinone      | Synechococcus elongates and Chlorella vulgaris | Herbicide removal | González-Barreiro et al. [173] |
|         |           |               |                | Thermosyneochococcus elongatus | Photosystem-II | Zimmermann et al. [184] |
| Sr. no. | Herbicide | Chemical name | Chemical family | Organism(s) | Parameter(s) studied | Reference |
|--------|-----------|---------------|----------------|-------------|----------------------|-----------|
| 28     | Trietazin (Tritazine) | 6-chloro-N,N,N,N9-triethyl-1,3,5-triazine-2,4-diamine | Triazine | Thermosyneochococcus elongatus | Photosystem-II | Broser et al. [137] |
| 29     | Irgarol | 2-methylthio-4-tert-butylamino-6-cyclopropylaminos-triazine | Triazine | Thermosyneochococcus elongatus | Photosystem-II | Zimmermann et al. [184] |
|        |           |               |                | Thermosyneochococcus sp. PCC 7942 | Growth, lipids and antioxidant | Deng et al. [100] |
| 30     | Bentazon | 3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide | Benzothiadiazole | Synechococcus elongatus PCC 7942 | Tolerance mechanism | Bagchi et al. [92 and 130] |
|        |           |               |                | Nostoc muscorum | Photosynthesis, photosynthetic pigments and respiration | Galhano et al. [94] |
|        |           |               |                | Anabaena cylindrica | Photosynthetic pigments, protein, carbohydrate, photosynthesis and respiration and antioxidant system | Galhano et al. [93 and 151] |
|        |           |               |                | Anabaena sp. | Photosynthetic pigments | Gulten and Onur [112] |
| 31     | Bromoxynil | 3,5-dibromo-4-hydroxybenzonitrile | Nitrile | Synechococcus elongatus | Biosensor | Kobiližek et al. [182 and 186] |
| 32     | Ioxynil | 4-hydroxy-3,5-diiodobenzonitrile | Nitrile | Synechococcus elongatus PCC7942 | Stress tolerance mechanism | Bagchi et.al. [92] and Kobiližek et al. [182 and 186] |
|        |           |               |                | Synechococcus elongatus | Biosensor | Zimmermann et al. [184] |
|        |           |               |                | Thermosyneochococcus elongatus | Photosystem-II | Tripathi et al. [69] |
| 33     | Diuron (DCMU) | 3-(3,4-dichlorophenyl)-1,1-dimethylurea | Urea | Nostoc muscorum | Growth and heterocyst formation | Vaishampayan [187] |
|        |           |               |                | Plectonema boryanum and Cyanophage LPP-1 | Growth Inhibition | Mallison and Cannon [71] and Zargar and Dar [80] |
|        |           |               |                | Anabaena, Nostoc and Oscillatoria | Growth and Nitrogen fixation | Preuss and Hall [181] |
|        |           |               |                | Synechococcus sp. | Biosensor | |
|        |           |               |                | Synechocystis sp. strain PCC 6893 | Herbicide Resistance | Narusaka et al. [127] |
|        |           |               |                | Synechococcus PCC7942. | Growth and photosynthesis | Tripathi et. al. [69] |
| Sr. no. | Herbicide | Chemical name | Chemical family | Organism(s) | Parameter(s) studied | Reference |
|--------|-----------|---------------|-----------------|-------------|----------------------|-----------|
| 13     |           |               |                 | Nostoc muscorum and Spirulina platensis | Biosensor | Shao et al. [179] |
|        |           |               |                 | Synechocystis sp. strain PCC 6803 | Biosensor | Kobilžek et al. [182 and 186] |
|        |           |               |                 | Synechococcus elongatus | Photosystem-II | Zimmermann et al. [184] |
|        |           |               |                 | Thermosynechococcus elongates | Photosynthetic energy dissipation | Deblis et al. [136] |
|        |           |               |                 | Microcystis aeruginosa, Synechocystis sp. and Synechococcus sp. | Photosynthetic pigments and photosynthesis | Singh et al. [56] |
|        |           |               |                 | Anabaena variabilis | Chlorophyll a, photosynthesis, respiration and heterocyst frequency | Singh et al. [56] |
|        |           |               |                 | Anabaena variabilis | Photosynthesis, antioxidant enzymes and DNA damage | Chen et al. [125] |
|        |           |               |                 | Anabaena sp. and Microcystis viridis | Fluorescence Kinetics | Deng et al. [110] Leunert et al. [74] |
|        |           |               |                 | Synechococcus sp. PCC 7942 | Growth, lipids and antioxidant enzymes | Safi et al. [176] |
|        |           |               |                 | Microcystis aeruginosa, Aphanizemenon flosaquae, Scenedesmus obliquus and Desmodesmus subsicus | Cyanobacterial Mat | Mellison and Cannon [71] |
|        |           |               |                 | Microcystis aeruginosa, Anabaena cylindrica, A. flosaquae and A. spiroides | Toxicity and biodegradation | Mansy and El-Bestawy [109] |
| 34     | Fluometuron | 1,1-dimethyl-3-(α,α,α-trifluoro-m-tolyl)urea | Urea herbicide | Plectonema boryanum and Cyanophage LPP-1 | Biodegradation | Safi et al. [176] |
|        |           |               |                 | Microcystis aeruginosa, Anabaena inaequalis and Chlorella kessleri | Growth Inhibition | Mellison and Cannon [71] |
|        |           |               |                 | Anabaena variabilis | Toxicity and biodegradation | Mansy and El-Bestawy [109] |
|        |           |               |                 | Microcystis aeruginosa, Anabaena inaequalis and Chlorella kessleri | Toxicity and biodegradation | Mansy and El-Bestawy [109] |
|        | Isoproturon | 3-(4-isopropylphenyl)-1,1-dimethylurea | Urea herbicide | Anabaena variabilis | Biodegradation | Mostafa and Helling [170] |
|        |           |               |                 | Microcystis aeruginosa, Anabaena inaequalis and Chlorella kessleri | Nitrogen metabolism | Aftab et al. [150] Aslim and Ozturk [70] |
| 36     | Linuron   | 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea | Urea herbicide | Chroococcus sp., Microcystis sp. and Synechococcus sp. Isolates | Toxicity | Aslim and Ozturk [70] Aslim and Ozturk [70] |
|        |           |               |                 | Microcystis sp., Synechocystis sp., Synechococcus sp. and Synechococcus sp. | Growth (Chlorophyll a) | Koksoy and Aslim [114] |
|        |           |               |                 | Nostoc muscorum | Growth and heterocyst | Vaishampayan [187] |
| 37     | Monuron   | 3-(4-chlorophenyl)-1,1-dimethylurea | Urea herbicide | Nostoc muscorum | Dry weight, protein and Chl a | Inderjit and Kaushik [117] |
| 38     | Propanil  | 3′,4′-dichloropropionanilide | Amide | Anabaena fertilissima | Dry weight, protein and Chl a | Inderjit and Kaushik [117] |
| Sr. no. | Herbicide   | Chemical name                                           | Chemical family     | Organism(s)                                                                 | Parameter(s) studied                        | Reference                          |
|--------|-------------|---------------------------------------------------------|---------------------|----------------------------------------------------------------------------|---------------------------------------------|------------------------------------|
| 39     | Tebuthiuron | 1-(5-tert-butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea | Substituted urea herbicide | Anabaena inaequalis, Aphanizomenon flos-aquae, Pseudoanabaena sp., Oscillatoria sp., Microcystis aeruginosa, Cyclotella meneghiana, Nitzschia sp., Scenedesmus quadricauda, Selenastrum capricornutum and Vibrio fisheri | 7-day carbon uptake                      | Peterson et al. [50]                |
| H      | Inhibitors of lipid synthesis |                                                            |                     | Anabaena, Nostoc and Nodularia                                                              | Growth and Nitrogen fixation                  | Okmen et al. [62]                  |
| 40     | Molinate    | S-ethyl perhydroazepine-1-thiocarboxylate               | Thiocarbamate       | Nostoc muscorum                                                              | Photosynthesis, photosynthetic pigments and respiration | Gaihano et al. [94]               |
|        |             |                                                        |                     | Anabaena cylindrica                                                           | Photosynthetic pigments, protein, carbohydrate, photosynthesis and respiration | Gaihano et al. [93]               |
|        |             |                                                        |                     | Nostoc muscorum                                                              | Antioxidant system and fatty acid profile    | Gaihano et al. [124]               |
| 41     | Thiobencarb (Benthiocarb) | S-4-chlorobenzyl diethyl(thiocarbamate) | Thiocarbamate       | Anabaena, Nostoc and Oscillatoria                                             | Growth and nitrogen fixation                  | Zargar and Dar [80]                |
|        |             |                                                        |                     | Nostoc muscorum                                                              | Growth, pigments and nitrogen fixation       | Bhunia et al. [106]               |
|        |             |                                                        |                     | Nostoc spatroides                                                             | Growth, photosynthetic pigment and photosynthesis | Xia, J [107]                     |
|        |             |                                                        |                     | Nostoc muscorum                                                              | Protein profiling, nitrogenase, glutamine synthetase, oxaloacetic acid transaminase and glutamic pyruvic transaminase activities | Dowidar et al. [144]              |
|        |             |                                                        |                     | Anabaena variabilis                                                          | Growth and photosynthesis                    | Battah et al. [188]               |
| I      | Inhibitor of 5-enolpyruvyl-shikimate-3-phosphate synthase (EPSP) |                                               |                     |                                            |                                     |                                   |
| 42     | Glyphosate  | N-(phosphonomethyl) glycine                            | Organophosphorus    | Synechocystis PCC6803 and Anabaena variabilis ATCC 29413                   | Tolerance limit and photosynthesis           | Powell et al. [59]                |
|        |             |                                                        |                     | Anabaena inaequalis, Aphanizomenon flos-aquae, Pseudoanabaena sp., Oscillatoria sp., Microcystis aeruginosa, Cyclotella meneghiana, Nitzschia sp., Scenedesmus quadricauda, | 7-day carbon uptake                      | Peterson et al. [50]                |
| Sr. no. | Herbicide | Chemical name | Chemical family | Organism(s) | Parameter(s) studied | Reference |
|---------|-----------|---------------|-----------------|-------------|---------------------|-----------|
|         |           |               |                 | *Selenastrum capricornutum* and *Vibrio fisheri* | Chlorophyll a fluorescence | Shikha and Singh [129] |
|         |           |               |                 | Wild and mutant strains of *Anabaena dolium* | Glyphosate degradation | López-Rodas et al. [61] |
|         |           |               |                 | *Spirulina* sp. | Herbicide tolerance and resistance | Forlani et al. [60] |
|         |           |               |                 | *Microcystis aeruginosa* | Herbicide Tolerance and mineralization |           |
|         |           |               |                 | *Anabaena sp.*, *Arthroseira fusiformis*, *Leptolyngbya boryanum*, *Microcystis aeruginosa*, *Nostoc punctiforme* and *spirulina platensis* | | |
|         |           |               |                 | *Anabaena fertiissima* | Dry weight, protein and Chl a | Inderjit and Kaushik [117] |
|         |           |               |                 | *Anabaena* sp. and *Microcystis viridis* | Photosynthesis, antioxidant enzymes and DNA damage | Chen et al. [125] |
|         |           |               |                 | *Scenedesmus quadricauda* and *Merismopedia glauca* | Growth, cell number, chlorophyll a, proteins and carbohydrates | Issa et al. [62] |
|         |           |               |                 | *Nostoc muscorum* | Toxicity | Singh et al. [102] |
|         |           |               |                 | *Microcystis wesenbergii* | Chlorophyll a fluorescence | Sun et al. [65] |
| J       | Inhibitor of phytoene desaturase (PDS) |               |                 | *Synechococcus* sp. PCC 7942 | Phytoene desaturase | Chamovitz et al. [189] |
| 43      | Fluridone | 1-methyl-3-phenyl-5-(α,α,α-trifluoro-m-toly)-4-pyridone | Not Known | *Synechococcus* sp. PCC 7942 | | Chamovitz et al. [189] |
| 44      | Norflurazon | 4-chloro-5-methylamino-2-(α,α,α-trifluoro-m-toly)pyridazin-3(2H)-one | Pyridazine | *Synechococcus* PCC7942 | Carotenoid biosynthesis | Chamovitz et al. [189] |
| K       | Inhibitor synthesis of very long chain fatty acids |               |                 | *Chloroacetamide* | Biodegradation | El-Nahhal et al. [174] |
| 45      | Acetochlor | 2-chloro-N-ethoxymethyl-6'-ethylacet-α-toluclidide | Chloroacetamide | *Nostoc muscorum, N. punctiforme, N. calciola, Anabaena variabilis, Gloeocapsa sp. and Aphanocapsa sp.* | Tolerance limit, protein, photosynthetic pigment, photosynthesis and nitrogen fixation | Singh and Datta [91 and 81] |
| 46      | Alachlor  | 2-chloro-2',6'-diethyl-N-methoxymethylacetanilide | Chloroacetamide | *Aphanizomenon flos-aquae, Pseudokirchnerella subcapitato, Daphnia magna, and D. longispina Anabaena variabilis* | Ecotoxicological impact | Abrantes et al. [190] |
|         |           |               |                 | | Growth, photosynthesis, | Singh et al. [27] |
| Sr. no. | Herbicide | Chemical name | Chemical family | Organism(s) | Parameter(s) studied | Reference |
|---------|-----------|---------------|-----------------|-------------|----------------------|-----------|
| 47      | Anilofos  | S-4-chloro-N- isopropylcarbaniloylmethyl O,O- dimethyl phosphorodithioate | Organophosphorus | *Nostoc muscorum, N. punctiforme, N. calcicola, Anabaena variabilis, Gloeocapsa sp. and Aphanocapsa sp.* | photosynthetic pigments, respiration, nitrogen fixation and GS activity | Singh and Datta [91 and 81], Singh et al. [90] |
|         |           |               |                 | *Nostoc muscorum* | Toxicity | Singh et al. [42] |
|         |           |               |                 | *Anabaena variabilis* | Growth, photosynthesis, photosynthetic pigments, respiration, nitrogen fixation and GS activity | Singh et al. [27] |
|         |           |               |                 | *Anabaena torulosa* | Tolerance, pigments, photosynthesis, nitrogen assimilation and antioxidants | Singh et al. [42] |
| 48      | Butachlor | N-butoxymethyl-2-chloro-2',6'-diethylacetanilide | Chloroacetamide | *Synechocystis* sp. strain PUPCCC 64 *Anabaena, Nostoc, Oscillatoria and Westiellopsis* *Nostoc muscorum, N. punctiforme, N. calcicola, Anabaena variabilis, Gloeocapsa sp. and Aphanocapsa sp.* | Tolerance and mineralization, tolerance, photosynthetic pigments and ammonia excretion, tolerance, photosynthetic pigment, photosynthesis and nitrogen fixation | Singh et al. [43], Selvakumar et al. [119] |
|         |           |               |                 | *Nostoc* | Photosynthetic pigments and photosynthesis | Singh and Datta [91 and 81], Singh et al. [90] |
|         |           |               |                 | *Aulosira fertilissima* | Photosynthetic pigments, photosynthesis and plasma membrane integrity | Kumari et al. [83] |
|         |           |               |                 | *Nostoc muscorum* | Protein profiling, nitrogenase, glutamine synthetase, oxaloacetic acid transaminase and glutamic pyruvic transaminase activities | Dowidar et al. [144] |
|         |           |               |                 | *Nostoc muscorum* | Toxicity | Singh et al. [91] |
|         |           |               |                 | *Anabaena variabilis* | Growth, photosynthesis, photosynthetic pigments, respiration, nitrogen fixation and GS activity | Singh et al. [27] |
| Sr. no. | Herbicide       | Chemical name                                              | Chemical family | Organism(s)                                           | Parameter(s) studied                               | Reference                                |
|---------|-----------------|------------------------------------------------------------|-----------------|-------------------------------------------------------|---------------------------------------------------|------------------------------------------|
| 49      | Menfenacet      | 2-benzothiazol-2-ylxyo-N-methylacetonilide                 | Oxyacetamide    | Plectonema boryanum                                   | GS activity                                       | Kumar and Vikash [118]                  |
|         |                 |                                                            |                 | Nostoc sp.                                            | Pigments and antioxidant                          | He et al. [84]                          |
|         |                 |                                                            |                 | Anabaena 7120, Anabaena doliolium and Anabaena LC31   | Photosynthetic pigments and fluorescence kinetics | Agrawal et al. [86]                       |
|         |                 |                                                            |                 | Anabaena variabilis                                   | Proteomics                                        |                                        |
|         |                 |                                                            |                 | Nostoc muscorum                                       | Nitrogen metabolism                               |                                        |
|         |                 |                                                            |                 | Nostoc muscorum                                       | Toxicity and Biodegradation                       | Aftab et al. [150]                      |
|         |                 |                                                            |                 | Nostoc muscorum                                       | Phospholipid fatty acid profiles                  | Annes et al. [85]                      |
| 50      | Metachlor       | 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methyl-ethyl)acylamide | Chloroacetamide | Plectonema boryanum and Cyanophage LPP-1              | Growth Inhibition                                 | Mallison and Cannon [71]               |
| 51      | Pretilachlor    | 2-chloro-2',6'-diethyl-N-(2-propoxyethyl)acetonilide        | Chloroacetamide | Nostoc muscorum                                       | Soil microbial communities                        |                                        |
|         |                 |                                                            |                 | Nostoc muscorum                                       | Phospholipid fatty acid profiles                  | Murata et al. [191]                    |
|         |                 |                                                            |                 | Anabaena fertilissima                                 | Dry weight, protein and Chl a                      | Inderjit and Kaushik [117]             |
|         |                 |                                                            |                 | Nostoc muscorum                                       | Toxicity                                          | Singh et al. [102]                     |
|         |                 |                                                            |                 | Anabaena variabilis                                   | 7-day carbon uptake and growth inhibition          | Peterson et al. [44]                   |
| L       | Photosystem-I electron diverters                            |                                                            |                 | Anabaena inaequalis, Aphanizomenon flos-aquae, Pseudoanabaena sp., Oscillatoria sp., Microcystis aeruginosa, Cyclotella meneghiana, Nitzschia sp., Scenedesmus quadricula, Selenastrum capricornutum and Duckweed | 7-day carbon uptake and growth inhibition          | Dragolova et al. [48]                  |
| 52      | Diquat          | 6,7-dihydrodipyrind(1,2-a:2',1'-c) pyrazine-5,8-dium       | Bipyridylum     | Anabaena variabilis and Plectonema boryanum           | Growth inhibition, alkaline phosphatase, proline, lipids, Biosensor Sorption | Shao et al. [180]                      |
|         |                 |                                                            |                 | Synechocystis sp. strain PCC 6803                     |                                                  | Kumar et. al. [177]                    |
|         |                 |                                                            |                 | Oscillatoria sp. dominated cyanobacterial mat          |                                                  |                                        |
|         |                 |                                                            |                 | Cylindrospermum raciborskii                            |                                                  | Leboulanger et al. [192]               |
| 53      | Paraquat       | 1,1'-dimethyl-4,4'-bipyridinium dichloride                   | Bipyridylum     | Anabaena oryzae and Nostoc elliposporum               |                                                  | Pandey et al. [49]                     |
|         | dichloride      |                                                            |                 |                                                      |                                                  |                                        |
| Sr. no. | Herbicide       | Chemical name                                                                 | Chemical family | Organism(s)                               | Parameter(s) studied                                      | Reference                        |
|--------|-----------------|--------------------------------------------------------------------------------|-----------------|-------------------------------------------|-----------------------------------------------------------|----------------------------------|
| M      | Inhibitors of 4-hydroxyphenyl-pyruvate dioxygenase (4-HPPD) |                                                                                  |                 |                                           |                                            |                                  |
| 54     | Mesotrione      | 2-(4-mesyl-2-nitrobenzoyl)cyclohexane-1,3-dione                               | Triketone       | Cyanobacterial community                  | Dose-response effects                                     | Singh et al. [102]               |
|        |                 |                                                                                  |                 |                                           |                                            |                                  |
| N      | Inhibitors of protoporphyrinogen oxidase (Protax) |                                                                                  |                 |                                           |                                            |                                  |
| 55     | Carfentrazone-ethyl (Shark) | ethyl (RS)-2-chloro-3-[2-chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorophenyl]proponate | Triazolone      | Nostoc spongiforme                        | Growth rate                                              | Crouzet et al. [175]             |
| 56     | Oxyfluoren      | 2-chloro-α,α,α-trifluoro-p-tolyl 3-ethoxy-4-nitrophenyl ether                  | Dipheneether     | Nostoc muscorum and Phormidium foveolarum | Tolerance, Growth, photosynthesis, nutrient uptake, nitrate reductase and alkaline phosphatase | Spencer et al. [89] Ravinderan et al. [96] Sheeba et al. [97] |
| 57     | Oxadiazon       | 5-tert-butyl-3-(2,4-dichloro-5-isoproxyphenyl)-1,3,4-oxadiazol-2(3H)-one       | Oxadiazolone    | Microcystis aeruginosa Synechocystis and Synechococcus | Photosynthetic energy dissipation | Deblios et al. [136] |
| O      | Membrane disruptor |                                                                                  |                 |                                           |                                            |                                  |
| 58     | Dinoseb         | 2-tert-butyl-4,6-dinitrophenol Dinitrophenol herbicide                          | Dinitrophenol herbicide | Synechocystis PCC 6803                    | Resistance, Biosensor                                    | Elanskaya et al. [165] Kobilžek et al. [182 and 186] |
Bensulfuron-methyl at low dose (0.1-1.0 ppm) stimulated the growth of Anabaena variabilis KJ-013 and Nostoc commune KJ-018 while high doses (8 and 10 ppm) caused more than 50% growth inhibition after 24 h of incubation [87]. Anabaena sp. and Nostoc sp. tolerated butachlor up to 30 ppm whereas Nodularia sp. was able to tolerate this herbicide up to 50 ppm [88]. Londox, a commercial form of bensulfuron-methyl at 0.028 ppm did not affect the growth of cyanobacterium Nostoc spongiforme when applied in combination with carfentrazone ethyl herbicide [89]. Nostoc muscorum, Nostoc calcicola, Aphanocapsa sp. and Gloeocapsa sp. tolerated anilofos (arozin) up to 5 ppm, Nostoc punctiforme up to 10 ppm and Anabaena variabilis up to 20 ppm [90 and 91]. Other reports showed that Oscillatoria simplicissima grew in Bensulfuron-methyl up to 40 ppm [41], Synechocystis sp. NUPCCC 64 up to 30 ppm [43] and Anabaena torulosa up to 10 ppm of anilofos [42]. Trifluralin (169-467 ppm) and linuron (0.038-0.441 ppm) caused 50% growth reduction in 10 cyanobacterial isolates belonging to Chroococcus, Microcystis, and Synechocystis (4) [70]. Wild and resistant strains of cyanobacterium Synechococcus elongatus PCC 7942 exhibited 50% survival when incubated in 30 and 150 µM bromoxylonil, respectively [92].

Effects of molinate and bentazon were studied on Anabaena cylindrica during a short-term experiment of 72 h [93]. The results revealed that both herbicides had a pleiotropic effect on the cyanobacterium at the range of 0.75-2 mM concentrations. Cyanobacterial growth was more adversely affected by molinate than bentazon. More than 50% growth inhibition was observed after 48 h treatment with 1.5-2 mM of molinate in A. cylindrica. Bentazon and molinate were also toxic to Nostoc muscorum with 72 h EC50 values being 22.7 and 1.2 mM, respectively [94]. In another study Sabater and Carrasco [95] obtained 96 h EC50 value of 13 ppm of molinate for this cyanobacterium. Cyanobacteria Paeudanabaena galeata, Anabaena sp., Nostoc and Nodularia sp. were able to tolerate molinate up to 100 ppm [88].

Oxyfluorfen (20 ppm) inhibited growth (50-67%) when measured in terms of protein content in four isolates of Oscillatoria [96]. Oxyfluorfen showed differential inhibitory effects on Nostoc muscorum and Phormidium foveolarum as indicated by decreased biomass production, photosynthetic pigments and photosynthetic activities. Exposure to 10 and 20 ppm oxyfluorfen caused reduction in dry masses by 41% and 50% in N. muscorum and only by 6% and 15% in P. foveolarum, respectively [97]. Ma et al. [40] in 96 h acute toxicity test demonstrated 50% growth reduction in Anabaena flosaquae, Microcystis flosaquae and Microcystis aeruginosa [40]. Exposure to 10 and 20 ppm diclofop caused reduction in dry biomass by 40-50% in Nostoc muscorum and by 6-15% in Phormidium foveolarum [97]. To explore the enantioselective effect of chiral herbicide dichlofop-methyl and its major metabolite dichlofop acid (DA), the physiological characteristics of Microcystis aeruginosa were investigated using biomass as growth parameter. Stimulation of biomass by R-DA and S-DA was apparent up to 5 ppm concentration. Ultra structural changes in gas vacuole, thylakoids, glycogen, cyanophycean granules, polyhedral bodies indicated different toxicity modes of these chemicals [98].

Lürling and Roessink [99] showed that Scenedesmus (green alga) out competed Microcystis (cyanobacterium) in the absence of herbicide metribuzin whereas the reverse was true in the presence of this herbicide. Herbicide irgarol (0.019 µM) was five times more toxic than diuron (0.097 µM) to Synechococcus sp. PCC 7942 as indicated by their EC50 values in a 96 h growth experiments [100]. A 96 h EC50 value of 7.71 ppm of irgarol for a marine cyanobacterium Chroococcus minor was observed [101]. Herbicide shark, a commercial form of carfentrazone ethyl, at 0.147 ppm did not affect the growth rate of Nostoc spongiforme [89]. The toxicity of thirteen herbicides to Nostoc muscorum has been studied using 94 h growth inhibition test by taking absorbance and chlorophyll a as growth parameters. The order of tolerance level of these herbicides was: 2,4 D > methyl metulsufuron > glyphosate > butachlor > atrazine > sulfosulfuron > metribuzin > pendimethalin > clodinafop propargyl > anilofos > cyhalofop butachlor > pretiachlor > paraquat dichloride. Further these results indicated that toxic effects of herbicides did not correlate with the nature, mode of action and class type of herbicide [102].

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3. PHOTOSYNTHETIC PIGMENTS

3.1 Chlorophyll a (Chl a)

Chlorophyll biosynthesis is catalysed by several enzymes in multiple steps [103,104]. The effect of different herbicides on Chl a synthesis in cyanobacteria varied due to differential nature and mode of action. Carotenoid inhibiting herbicide fluridone inhibited Chl a pigment in Oscillatoria agardhii in a dose dependent manner [105]. Thiobencarb (2-6 ppm) reduced the Chl a content in Nostoc muscorum by 56-97% and it was suggested that the low pigment may be as a result of photo oxidation arising from inability of Chl a to dissipate its absorbed excitation energy when electron transport was inhibited by herbicide [106]. While other studies demonstrated that thiobencarb (2-10 ppm) did not affect significantly the Chl a pigment in Nostoc sphaeroides [107].

Atrazine (10-100 ppb) inhibited Chl a pigment of Oscillatoria limnetica, Arthrosira sp., and Synechococcus sp. [53,108]. Sub-lethal concentration of pure (6 ppm) and formulated form (2 ppm) of atrazine and DOMU (0.4 and 0.5 ppm) inhibited Chl a content by 74-80% in wild type and 68-77% in multiple herbicide resistant strain of cyanobacterium Anabaena variabilis [56]. Flumeturon (140-1400 ppm) caused reduction in Chl a pigment in time and dose dependent manner in six cyanobacterial strains belonging to Microcystis aeruginosa, Anabaena cylindrica, Anabaena flosaquae and Anabaena spiroides, with complete inhibition after 2-3 days of exposure. The inhibition of Chl a content was species specific. The order of affected species at highest tested dose was: Anabaena spiroides > Microcystis aeruginosa (11) > Microcystis aeruginosa (15) > Microcystis aeruginosa (1) > Anabaena cylindrica > Anabaena flosaquae [109].

Monosulfuron (0.008-800 ppm) exerted its effect on Chl a of Anabaena flosaquae in a dose dependent manner under 2000-4000 lux light intensity. Chl a synthesis was more sensitive under 2000 lux light intensity than other light intensities [76]. The herbicide also exhibited a dose dependent reduction in Chl a of Anabaena flosaquae in presence of different nitrogen contents. The content of Chl a was reduced by 47-73% in presence of 0.05 ppm nitrogen and 85-97% in 0.8 ppm nitrogen after treatment with monosulfuron (0.016-0.30 ppm) for 144 h indicating synergistic effect [77].

Yan et al. [110] observed increased Chl a content (17-62%) in Anabaena sphaerica after 6 days treatment with 5-50 ppm molinate under 300-3000 lux light intensity. While Kobbia et al. [111] verified reduction in Chl a content in Anabaena variabilis at all the tested concentrations (0.2-0.8 ppm) of molinate. The effects of commercial formulations of two selective herbicides molinate (Ordham) and bentazon (Basagran) recommended for integrated weed management (IWM) on rice were laboratory assessed on Anabaena cylindrica during a short-term experiment of 72 h [93]. The results revealed that both herbicides had a pleiotropic effect on the cyanobacterium at the range of concentrations tested (0.75-2 mM). The same authors also reported that molinate (2 mM) inhibited Chl a (20%) in Nostoc muscorum after 72 h treatment as a result of degradation of lipid complex associated with pigments in thylakoids [94]. Xia [107] demonstrated that 10 ppm of thiobencarb had insignificant effect on Chl a synthesis of Nostoc sphaeroides. The constant level of Chl a content of Nostoc muscorum culture exposed to bentazon (0.75-2.0 mM) demonstrated that herbicide had no effect on this photo pigment [93]. While comparing the Chl a content of two strains of Anabaena isolated from Turkey rice fields, Gulten and Onur [112] reported that bentazon (100 ppm) inhibited Chl a content severely in Anabaena sp. GO10 than Anabaena sp. GO4.

Low concentration (1 mM) of 2,4 D and MCPA did not affect the Chl a synthesis in Anabaena UAM 202 while higher dose (10 mM) of both herbicides completely degraded Chl a after 48 h treatment [66]. 2,4 D (5-20 ppm) inhibited Chl a synthesis by 30-52% in immobilized Nostoc muscorum, Nostoc punctiforme, Nostoc calcicola, Anabaena variabilis, Aphanocapsa sp., and Gloeocapsa sp. [91]. The decrease in Chl a content by 60-77% was reported in Anabaena fertilissima, Aulosira fertilissima and Westiellopsis prolifica after treatment with 60-120 ppm of 2,4 D was reported [113]. Koksy and Aslim [114] reported inhibition of Chl a by 2,4 D (123-748 ppm), trifluralin (139-882 ppm) and linurin (0.02-0.77 ppm) in several strain of cyanobacteria.

Anilofos (10 ppm) enhanced Chl a synthesis in Anabaena variabilis ARM310 [115]. The commercial formulation of anilofos, arozin at IGC50 concentration severely affected Chl a in Nostoc muscorum, Gloeocapsa sp. and Aphanocapsa sp. as compared to Anabaena.
variabilis, Nostoc punctiforme and Nostoc calcicola [90]. Immobilized forms of Nostoc muscorum, Nostoc punctiforme, Nostoc calcicola, Anabaena variabilis, Aphanocapsa sp., and Gloeocapsa sp. exhibited a reduction in chl a (44-67%) when treated with at IGC_{50} dose of anilofos [91]. Treatment with anilofos (10-20 ppm) for 6 day caused a reduction in Chl a content by 18-47% in Oscillatoria simplicissima [41] while a decrease of 21-60% in chl a content of Synechocystis sp. PUPCCC 64 by 5-20 ppm [43] and by 21-43% in Anabaena torulosa with 1.25-5.0 ppm anilofos [42] was reported.

Penoxasulam, an acetolactate synthesis inhibiting herbicide, at 100 ppb reduced Chl a by 90% in Anabaena sp. and 58% in Pseudanabaena limnetica but did not affect noxious cyanobacterium Microcystis aeruginosa [116]. Propanil (0.187-1.5 ppm) and glyphosate (10-80 ppm) also suppressed Chl a production by 5-38% in Anabaena fertilissima, while pretialachor (5-40 ppm) exhibited 10-45% reduction in Chl a content [117]. Alachlor (15-20 ppm) and butachlor (10-20 ppm) caused a decrease (27-47%) in Chl a content in immobilized cyanobacteria Nostoc muscorum, Nostoc punctiforme, Nostoc calcicola, Anabaena variabilis, Aphanocapsa sp., and Gloeocapsa sp. [91]. When the wild type and MHR strain of Anabaena variabilis were exposed to 10-100 ppm each of alachlor, arozin, butachlor and 2,4 D, the wild type exhibited 42-58% reduction in Chl a content while MHR strain showed 65-72% decrease [27]. Chl a content in Plectonema boryanum sharply declined (40%) in five day treatment with 40 ppm butachlor [118]. The dose dependent reduction in Chl a of Merismopedia glauca by glyphosate (37-150 ppm) was observed by Issa et al. [62]. Butachlor considerably declined Chl a in Aphanocapsa, Anabaena fertilissima, Anabaena variabilis, Gloeocapsa, Nostoc sp., Nostoc punctiforme, Nostoc calcicola, and N. muscorum [82-84, 91]. Other studies have revealed that butachlor at 3-12 ppm concentrations affected Chl a production in strains of Anabaena, Nostoc and Oscillatoria sp. but did not effect Chl a of Westiellopsis strains [119]. Fenoxaprop-p-ethyl (6.25 ppm) stimulated Chl a contents in Anabaena sp. GO10. Further, increasing herbicide concentrations suppressed Chl a synthesis in a dose dependent manner. Chl a contents was completely suppressed by 100 ppm of fenoxaprop. Another herbicide cyhalofop-butyl at 25 ppm partly stimulated this pigment in this cyanobacterium but pigment synthesis was completely inhibited at 400 ppm fenoxaprop [120].

3.2 Phycobiliproteins

Phycobiliproteins (PBS) are major light harvesting pigments and reserve of nitrogen in cyanobacteria [121] and it has been shown that these pigments are also affected by herbicides. The differential response of PBS to herbicides may be due to their exterior distribution on thylakoid membrane of cyanobacteria and thus direct contact with herbicides. Carotenoid inhibiting herbicide fluoridine did not exhibit inhibitory effect on phycocyanin in filamentous non-heterocystous cyanobacterium Oscillatoria up to 100 ppb [105]. The phycocyanin (PC), phycoerythrin (PE) and allophycocyanin (APC) content in Nostoc sphaeroides significantly declined (60%) on exposure to 10 ppm thiobencarb [107]. Monosulfuron (0.008-0.08 ppm) exerted stimulatory effect on PBS (increased by 11-46%) of Anabaena flosaquae but exhibited inhibitory effect (decreased by 33-98%) at higher concentrations (0.8-800 ppm) of herbicide when exposed to varied light intensities (2000, 3000 and 4000 lux). Further, these biliprotein were more sensitive to herbicide at 2000 lux light intensity than other light intensities [76]. Treatment of Aulosira fertilissima with butachlor (65 µM) for 15 days showed severe inhibition in synthesis of APC (75%) followed by APC (50%) and PE (49%) [83]. The effect of monosulfuron on PBS of Anabaena flosaquae grown in presence of nitrogen source displayed dose dependent affect. Exposure to monosulfuron (0.016-0.30 ppm) in presence of three nitrogen concentrations (0.05-0.8 ppm), the content of biliprotein decreased by 10-37% compared to control cultures [77].

The sub-lethal doses of pure and formulated forms of atrazine and DCMU reduced PC (73-79%) and PE (66-71%) content on day 8 in both wild type and MHR strain of Anabaena variabilis [56]. Phycobilipins were adversely affected by 2,4 D than Chl a and carotenoids in Anabaena fertilissima, Aulosira fertilissima and Westiellopsis prolifica [113].

Commercial formulation of anilofos, arozin (5-20 ppm) inhibited PC and PE content in range of 53-71% and 57-83%, respectively, in immobilized Nostoc muscorum, Nostoc punctiforme, Nostoc calcicola, Anabaena variabilis, Aphanocapsa sp., and Gloeocapsa sp. [91]. Anilofos (10-20 ppm) decreased PC content by 14-36%, APC by
12-32% and PE by 15-37% on day 6 in Oscillatoria simplicissima [41]. In diazotrophic cyanobacterium Anabaena torulosa, anilofos (1.25-5.0 ppm) decreased PC content by 20-50%, APC by 17-46% and PE by 14-48% [42]. Treatment of Synechocystis sp. PUPCCC 64 with 5-20 ppm anilofos for six days caused a loss of PC APC and PE by 55-99%, 25-85% and 47-80%, respectively [43].

Alachlor (15-20 ppm) decreased PC and PE content in the range of 29-75%, in Ca-alginate immobilized Nostoc muscorum, Nostoc punctiforme, Nostoc calcicola, Anabaena variabilis, Aphanocapsa sp., and Gloeocapsa sp. whereas butachlor (10-20 ppm) caused 59-81% reduction. 2,4 D (5-20 ppm), on the other hand reduced PC and PE content in the range of 30-88% in these cyanobacteria [91]. Total PBS content was more adversely affected by commercial formulations of molinate than bentazon in Anabaena cylindrica [93]. Gülten and Onur [112] compared the phycobilins of two species of Anabaena isolated from Turkey paddy fields and found that inhibition of these pigments was more pronounced in Anabaena sp. GO10 than GO4 when treated with 100 ppm bentazon.

Butachlor (3-12 ppm) significantly reduced phycobiliproteins (PBPS) in Anabaena, Nostoc and Oscillatoria strains but did not affect PBPS of Westiellopsis [119]. A reduction in PBPS content in Anabaena dolitulium by machete was reported by Kashyap and Pandey [122]. Chen et al. [82] showed that PC and APC content significantly increased when Ge–Xian–Mi (Nostoc) colonies were treated with 10 µM butachlor, but contents declined with further increase in butachlor concentration. Kumari et al. [83] observed a dose-dependent rise in PE, APC and PC of A. fertilissima cells, while He et al. [84] reported the decline in PBPS content in Nostoc sp. in presence of butachlor. Fenoxaprop-p-ethyl (6.25 ppm) stimulated PBPS in Anabaena sp. GO10. Further, increase in herbicide concentrations suppressed PBPS synthesis in a dose dependent manner. The PBPS was completely suppressed by 100 ppm of fenoxaprop. Other herbicide cyhalofop-butyl at 25 ppm partly stimulated PBPS in this cyanobacterium but completely repressed at 400 ppm concentration [120].

### 3.3 Carotenoids

Carotenoids are the essential pigments which protect the photosynthetic system from oxidative damage by stressors such as herbicides [123]. Carotenoids in non-nitrogen fixer Oscillatoria agadhai were severely inhibited by herbicide fluridone up to 100 ppb [105]. The carotenoid synthesis in this organism, exposed to 4000 lux light, was more sensitive to herbicide compared to other light intensities. Monosulfuron (0.008-0.08 ppm) reduced carotenoid production in Anabaena flosaquae by 28-90% when colonies were exposed to 3000 and 4000 lux light intensity after 144 h treatment [76]. Treatment for 8 days with sub-lethal doses of pure and formulated forms of atrazine and DCMU exhibited reduction in carotenoids synthesis (40-47%) in both wild type and MHR strain of Anabaena variabilis [56]. The production of carotenoid by Anabaena flosaquae was inhibited synergistically with increase in both nitrogen and monosulfuron concentrations. The content of carotenoids in cells of A. flosaquae was reduced by 31-100% when exposed to 0.05-0.8 ppm nitrogen and 0.016-0.3 ppm monosulfuron [77]. Carotenoids of Anabaena cylindrica were more adversely affected by commercial formulations of molinate (ordham) than bentazon (basagran) at 0.75-2.0 mM concentration [93]. Molinate (0.75-2.0 mM) after 72 h of treatment drastically inhibited carotenoids (96-98%) in Nostoc muscorum [124].

The carotenoid synthesis in diazotrophic Anabaena fertilissima, Aulosira fertilissima and Westiellopsis prolifica was affected in a time and dose dependent manner by 2,4 D. At the end of experiments after 16 days, carotenoids in Anabaena fertilissima were depleted by 80% at 60 ppm of 2,4 D. However, carotenoid content was decreased by 64% at 120 ppm in W. prolifica followed by A. fertilissima where reduction was 72% relative to control [113]. Treatment with anilofos (10-20 ppm) for 6 days caused more than 53% inhibition in synthesis of carotenoids in non-heterocystous Oscillatoria simplicissima [41], 26-45% reduction by 1.25-5.0 ppm in Anabaena torulosa [42] and 32-90% reduction by 5-20 ppm of herbicide in Synechocystis sp. PUPCCC 64 [43].

The addition of 10 µM each of glyphosate and MCPA significantly decreased the carotenoid content in UV irradiated cells of Microcystis novaci and Anabaena sp. while the addition of DCMU (10 µM) did not affect carotenoids in these cyanobacteria [125]. Compared to untreated control cultures, sub-lethal doses of pure and formulated forms of atrazine (2 and 6 ppm) and DCMU (0.4 and 0.5 ppm) reduced...
carotenoids by 40-47% on day 8 in wild type and MHR strain of Anabaena variabilis [56]. Five days exposure to 40 ppm butachlor sharply declined (70%) carotenoids in Plectonema boryanum [118]. Fenoxaprop-p-ethyl (6.25 ppm) stimulated β-carotene in Anabaena sp. GO10. Further, increase of herbicide suppressed this pigment in a dose dependent manner. The β-carotene was completely suppressed by 100 ppm of fenoxaprop. Herbicide cyhalofop-butyl at 25 ppm partly stimulated β-carotene in this cyanobacterium but completely repressed at 400 ppm concentration [120].

4. PHOTOSYNTHESIS

The inhibition of pigment synthesis by alteration in pigment synthesizing enzymes or due to different mode of action of herbicides results in alteration in photochemical activity which may disturb the light harvesting complex or energy transfer within photosystems which ultimately affect photosynthesis [97,126]. Thus, the response of cyanobacteria varied with type and nature of herbicide used. Atrazine was more toxic than its metabolites towards photosynthesis of cyanobacteria Anabaena inaequalis, Anabaena cylindrica, Anabaena variabilis and green algae Chlorella pyrenoidosa and Scenedesmus quadricauda with EC50 values ranging from 0.1 to 0.5 ppm [35]. The supplementation of atrazine (1000 ppm) in growth medium marginally affected photosynthetic rate (10% of control) in resistant SG2 cyanobacterial strains falls of Synechocystis/Pleurcapsa/Microcystis group and had no effect on growth rate. However, more than 89% inhibition in photosynthesis was observed in Synechocystis sp. strain 6803 [73]. This is in contrast to results of Narusaka et al. [127] who showed that several herbicide resistant mutants of Synechocystis sp. strain PCC 6803 which grew slower under photosynthetic growth conditions and evolved 70% less oxygen than control strain grown under herbicide free conditions. Interestingly, Dalla-Chiesa and co-workers [128] reported that mutation in the D1 protein in serine 264 to proline 264 of Synechocystis sp. strain PCC 6803 allowed the strain to grow photoautotrophically and slightly resistant to atrazine, but oxygen evolution was only 60% of that of wild-type control 659 strain. The treatment of carotenoid inhibiting herbicide fluridone up to 100 ppb inhibited photosynthesis in light saturated cells of Oscillatoria agardhii [105]. Exposure to atrazine for 72 h at EG50 doses to ten species of green algae, cyanobacteria and diatoms resulted in significant inhibition of photosynthetic activities of all phytoplankton species acclimated to low to high light conditions. Inhibition of PS-II quantum yield varied between different groups of algae. Data showed that 50% inhibition in quantum yield of PS-II was observed at 315 nM and 282 nM atrazine for diatoms and green algae, respectively, while 50% inhibition in quantum yield of PS-II of cyanobacteria were caused by 102 nM of atrazine [58].

The photosynthetic activities of Nodularia and Nostoc treated with 2,4 D or MCPA at 1 mM were not affected while were inhibited significantly with higher concentrations of herbicide. Addition of 2,4 D at 10 mM to cultures resulted in 80% inhibition in photosynthesis while the effect of MCPA was more severe in a way that the cells began to consume oxygen in presence of light [66]. Photosynthetic electron transport (Hill activity) and oxygen evolution in both wild type and mutant cells of Anabaena dolioium were stimulated by glyphosate (50-200 ppm) but exhibited extreme inhibition by high concentrations (200-400 ppm) of herbicide [129]. Thiodencarb at 10 ppm decreased photosynthesis by nearly 50% in Nostoc sphaeroides [107]. Over 50% inhibition in photosynthesis was observed in Anabaena variabilis and Nostoc commune, when 8 to 10 ppm bensulfuron-methyl was applied to cultures [87].

Mutant strain (Mu1) of Synechococcus sp. PCC 7942 exhibited superior photosynthetic activities in presence of butachlor under regular growth conditions compared to wild type. Further, Mu1 had an increased expression of PsbO at mRNA and protein level and PsbO was tightly bound to Photosystem II, relative to wild type [130]. The effects of the commercial bentazon (basagran) and molinate (ordham), recommended for IWM on rice, were laboratory assessed on Anabaena cylindrica in a short-term experiment of 72 h. The results revealed that photosynthesis was inhibited in a time and dose-response manner and higher concentrations of ordham fully stopped O2 evolution after 48 h [93].

Butachlor and fluchloralin exerted little effect on photosynthetic oxygen evolution in Nostoc muscorum and Gloeocapsa sp. whereas propanil severely inhibited oxygen evolution in both the organisms [131,132]. Exposure of wild type and multiple herbicide resistant (MHR) strain of Anabaena variabilis to 10-100 ppm of alachlor,
arozin, butachlor and 2,4 D, led to the inhibition of photosynthesis by 41-61% at 15 ppm and by 50-55% at 80 ppm, respectively [27]. In another study, butachlor (65 μM) treatment to Aulosira fertilissima for 15 days decreased photosynthesis, PS-I, PS-II and whole chain activity by 24-48% [83]. Butachlor at LC50 dose significantly inhibited PS-I, PS-II and whole chain activities of three species of Anabaena. These activities declined in the range of 33-40% after one day treatment which recovered gradually in subsequent days in Anabaena sp. PCC 7120, while A. dolioolum and Anabaena LC31 exhibited continuous decrease with time [86]. Application of monosulfuron at 0.001-10 ppm exerted an inhibitory effect on photosynthesis in three nitrogen fixing cyanobacteria Anabaena azollae, A. flosaquae, and A. azotica leading to a lower net photosynthetic rate and a smaller Fv/Fm ratio as revealed by chlorophyll a fluorescence studies [133]. DCMU (5 ppm) inhibited oxygen evolution by 75% in cyanobacterial strain SG2 of Synechocystis/Pleurocapsa/Microcystis group as reported by Sajjaphan et al. [73]. DCMU treated wild type (0.4 ppm) and MHR strain (0.5 ppm) of Anabaena variabilis showed 80-87% inhibition in photosynthetic O₂ evolution compared to untreated control cultures [56].

The study of Guanzon and Nakahara [134] revealed that Microcystis aeruginosa evolved 50% less oxygen when treated with 8.4x10⁴ ppb p-nitrophenyl 2,4,6-trichlorophenyl ether compared to untreated control. Anilofos (1.25-5.00 ppm) decreased photosynthetic oxygen evolution by 15-57%, PS-I and PS-II activity by 18-61% and 25-75%, respectively, and whole chain activity by 25-75% in Anabaena torulosa [42]. Issa et al. [62] showed stimulation of photosynthetic activity in Merismopedia glauca by simazine (37-150 ppm) in a dose dependent manner. Inhibition of photosynthesis was maximum at IGCso concentration of 2.4 D in Nostoc muscorum followed by Gloeocapsa sp. and Aphanocapsa sp. [81]. However, in Gloeocapsa sp. and Anabaena UAM202 photosynthesis was inhibited at higher concentration of 2.4 D [66,67]. Photosynthetically driven oxygen evolution was 10% less in resistant strain of Synechocystis strain SG2 while wild strain exhibited 90% inhibition in oxygen evolution in presence of 2.4 D [73]. The rate of photosynthesis in the unicellular cyanobacterium Synechococcus aeruginosus, isolated from rice field of India, declined in time and dose dependent manner in the presence of high concentrations (500-1000 ppm) of 2,4 D [135]. Sheeba et al. [97] reported reduction in photosynthesis, PS-I, PS-II and WCA in Nostoc muscorum and Phormidium foelovarum in presence of 2,4 D with more pronounced effect on former species than later one. When exposed to diuron, the quantum yield of PS-II in Synechocystis sp. and Microcystis aeruginosa decreased while oxadiazon (2.89 μM) decreased PS-II quantum yield only in Synechocystis sp. [136].

Broser et al. [137] presented the first crystal structure of PS-II with bound herbicide terbutryn. The crystallized PS-II core complexes were isolated from the thermophilic cyanobacterium Thermosynechococcus elongatus. The herbicide terbutryn was bound via at least two hydrogen bonds to the Q(B) of reaction centers. Herbicide binding to PS-II further influenced the redox potential of Q(A), which is known to affect photoinhibition.

5. NITROGEN METABOLISM

5.1 Nitrogen Fixation

Butachlor, fluchloralin and propanil did not affect nitrogenase activity of Nostoc muscorum but in Gloeocapsa sp. caused stimulation in nitrogen fixation [131]. Nitrogenase activity of Nostoc G3 was completely inhibited in presence of golfix (50 and 100 ppm), arelon (15 and 30 ppm), paraquat (10 and 20 ppm) and 1 μM DCMU [138]. Nitrogen fixing capacity of Anabaena inaequalis and Anabaena cylindrica was sensitive to atrazine and its degradation products. Fifty percent reduction in nitrogen fixation was observed with all compounds at more than 100 ppm with the exception of atrazine when tested towards A. inaequalis which gave 50% inhibition at 55 ppm [54]. Low concentration of 2,4 D (1 and 10 ppm) stimulated nitrogen fixation in all the strains of Anabaena while higher dose (100 ppm) inhibited nitrogen fixation in strain ARM 299, ARM 308 and ARM 311 [139]. In another study, cultures of Nostoc muscorum ISU exhibited 2 fold inhibition in nitrogenase activity at IGCso concentration of 2.4 D followed by Gloeocapsa sp. and Aphanocapsa sp. However, such reduction in nitrogenase activity in Gloeocapsa sp. and Anabaena UAM202 was found at much higher concentration 175 ppm and 10 mM, respectively [66,67].
Alachlor (80 ppm) completely inhibited nitrogen fixation in *Anabaena doliolium*, *Nostoc muscorum* and *Aphanotohece stagnina* [140]. Butachlor enhanced the growth of *Anabaena sphaerica* and accelerated nitrogen fixation [141]. Alachlor and butachlor at IGC50 concentration (10-15 ppm) exhibited substantial inhibition in nitrogen fixation in *Nostoc muscorum*, *Gloeocapsa* sp. and *Aphanocapsa* compared to *Anabaena variabilis*, *Nostoc punctiforme* and *Nostoc calcicola* [81]. Likhitkar and Trar [142] reported partial inhibition in nitrogenase activities at 200 ppm of butachlor in *Nostoc commune* and *Nostoc muscorum*.

Isopropyl salt of glyphosate caused significant inhibition in nitrogen fixation by *Anabaena variabilis* compared to free acid. The free acid form of glyphosate had no effect on nitrogen fixation even at 20 mM whereas 5 mM of isopropylamine salt caused 50% inhibition [59]. Nitrogenase activity of *Anabaena variabilis* decreased by 94-98% and by 85-86% in *Nostoc commune* after 24 h of incubation with 10 ppm and 20 ppm of bensulfuron-methyl, respectively [87]. Molinate at 100 ppm inhibited nitrogen fixing capacity of *Anabaena* sp., *Nostoc* and *Nodularia* sp. [88].

Shaaban Dessouki et al. [143] observed that low concentration of thiobencarb (1 ppm) enhanced nitrogenase activity of *Nostoc kihlmani* and *Anabaena oscillatoriodes* while higher concentration was inhibitory. Butachlor (2-20 ppm) exhibited significant reduction in nitrogenase activity (2-54%) of *Nostoc muscorum* than thiobencarb which at 5 and 8 ppm concentrations caused a reduction of 16 and 32%, respectively [144]. Okmen and Ugur [145] compared the effect of herbicide bispyricydm on nitrogen fixing capacity of ten cyanobacterial isolates belonging to *Anabaena*, *Gloeotheca* and *Synechocystis*. Nitrogen fixation was completely inhibited by 100 ppm of bispyribac in *Synechocystis* sp. while in other cyanobacteria 500 ppm bspyribac was effected. The reduction in nitrogen fixation in cyanobacteria by herbicides may be due to low photosynthetic rate [93,107,146] which provides reductant and ATP to nitrogenase and carbon skeleton to fix nitrogen [147,148].

Arozin (10 ppm) has been reported to enhance nitrogenase activity in *Anabaena variabilis* ARM 310 [115]. Likhitkar and Trar [142] reported partial inhibition of nitrogenase activity in *Nostoc commune* and *Nostoc muscorum* at 200 ppm of butachlor. *Nostoc muscorum* ISU, *Gloeocapsa* sp. and *Aphanocapsa* sp. also exhibited substantial inhibition in nitrogenase activity as compared to *A. variabilis*, *N. punctiforme* and *N. calcicola* at IGC50 concentration of butachlor and alachlor [81]. When wild type and MHR strain of *Anabaena variabilis* were exposed to 10-100 ppm alachlor, arozin, butachlor and 2,4 D, the wild type at 15 ppm of all the herbicides exhibited 75-95% nitrogenase activity while MHR strain at 80 ppm of these herbicides exhibited 65-70% nitrogenase activity [27].

5.2 Nitrogen Uptake and Its Assimilation

Cyanobacteria use nitrate, nitrite and ammonium as nitrogen source for growth and development. Scanty reports are available on effect of herbicides on nitrogen source uptake and its assimilation by cyanobacteria. The uptake of nitrate and ammonium was inhibited by Machete and Saturn in *Nostoc* sp., *Nostoc calcicola* and *Anabaena doliolium*. However, 2,4-D (100 ppm) stimulated the uptake of nitrate but not of ammonium but higher doses of 2,4-D inhibited the uptake of both nitrogen sources [79]. Ethyl ester salt of 2,4 D (15-60 ppm) inhibited nitrate reductase and glutamine synthetase activities in a dose dependent manner in *Anabaena fertilissima*, *Aulosira fertilissima* and *Westiellopsis prolifica* [113]. Singh et al. [149] reported that 30 µM of glyphosate inhibited ammonium uptake by *Nostoc muscorum* but the authors did not mention which formulation of glyphosate was used. Nitrate uptake by *Nostoc muscorum* and *Phormidium foveolarum* decreased after exposure to oxyfluorfen (10 and 20 ppm) and UV-treatment. Further, oxyfluorfen alone and together with UV-B drastically decreased NR activity in *N. muscorum* however NR activity increased in *P. foveolarum* [97].

Treat ment with anilofos (5 ppm) for 12 h caused 12% reduction in nitrate and 28% reduction in ammonium uptake with 22% inhibition in glutamine synthetase activity in *Anabaena torulosa*. The decrease in photosynthetic rate by anilofos may probably have caused low rate of nitrate uptake. Interference of herbicide with membrane potential of cyanobacterium may have caused low uptake of ammonium which further reduced GS activity due to less availability of ammonium [42]. Herbicides isoproturon and butachlor at 10 µM inhibited nitrate and nitrite uptake in time dependent manner in *Anabaena variabilis* up to 24 h treatment. Further, nitrate and nitrite reductase activities of this cyanobacterium were also inhibited [150].
6. STRESS TOLERANCE MECHANISM

Toxicity of herbicides may lead to the generation of free radicals and cyanobacteria may respond to this stress by inducing enzymatic as well as non enzymatic antioxidant mechanism [42,43,124,151]. Superoxide dismutase (SOD) is involved in the neutralization of highly reactive oxygen species (ROS) such as superoxide radicals and singlet oxygen resulting in the generation of the lesser toxic hydrogen peroxide (H₂O₂). H₂O₂ is still harmful to cells requiring removal by catalase (CAT) and/or peroxidase (POD) enzymes [123].

6.1 Enzymatic Antioxidant System

Few reports are available in literature on the response of enzymatic antioxidant system of cyanobacteria to herbicides. Bentazon induced oxidative stress is a manifestation of multistep reactions, resulting in membrane damage leading to the production of free radicals which may be scavenged by antioxidant enzymes such as SOD, CAT and POD. Galhano et al. [151] reported significant increase in SOD (13-15%), POD (20-188%) and CAT (35-46%) activities in a time- and dose-dependent manner in Anabaena cylindrica when treated with bentazon (0.75-2 mM). Anilofos (20 ppm) caused 3 fold increase in SOD, 2 fold increase in POD and 2.8 fold increase in CAT activities in Oscillatoria simplicissima [41] while the activity of these enzymes increased by 1.8-3.5 fold in Anabaena torulosa after treatment with 1.25 - 5 ppm of herbicide [42]. The stimulation SOD (137-180%), POD (104-174%) and CAT (109-131%) activities over control by 5-20 ppm of the same herbicide in another cyanobacterium Synechocystis sp. PUPCCC 64 has also been reported [43]. Contrary to these reports, molinate (0.75-2.0 mM) decreased the activity of SOD (34-92%), POD (70-88%) and CAT (25-95%) in a time and concentration dependent manner in Nostoc muscorum [124].

In bloom forming Microcystis novaci and nitrogen fixing Anabaena sp. cultures, the addition of DCMU (10 µM) did not have significant effect on SOD activity in the UV-B irradiated cells however the addition of glyphosate and MCPA decreased SOD activity compared with UV treatment alone and the activity was not restored even after glyphosate and MCPA were removed during recovery process [125]. Wild strain of Synechococcus elongatus PCC 7942 showed an downward trend of SOD and POD activity whereas resistant strain exhibited increasing trend (increased by 2-3 folds) with treatment of 150 µM bromoxynil [92]. To determine whether diclofop acid and its enantiomers affected antioxidants of Microcystis aeruginosa, the activity of SOD was determined after treatment with 1-5 ppm of herbicide. After 48 h exposure, all the species of herbicide increased SOD activity. Diclofop acid (1-5 ppm) increased activity by 1.3-1.53 folds whereas S-enantiomers increased the activity of SOD by 1.91-3.41 folds [152]. The increase in the level of free radicals by butachlor (5-40 ppm) in a five day experiment triggered the production of SOD, POD and CAT in a dose dependent manner in Plectonema boryanum [118]. Butachlor at 40 and 80 ppm enhanced the activities of SOD, CAT, POD and GR significantly in Nostoc sp. [84]. Oxyflurafen (10 ppm) alone increased level of SOD and CAT in Nostoc muscorum, however, when oxyflurafen treatment was combined with UV-B, the activities of these enzymes decreased. On the other hand, in Phormidium foveolarum only 20 ppm oxyflurafen could cause a decrease in CAT activity and 20 ppm herbicide along with UV-B decreased POD activity as well [97].

Irgarol 1051 (0.01 µM) and diuron (0.09 µM) greatly enhanced CAT activity in Synechococcus sp. PCC 7942 which gave evidence of enhanced free radical production under herbicide stress. However, the suppression of CAT activity under high concentrations of Irgarol 1051 (>0.01 µM) and diuron (>0.09 µM) indicated that antioxidant defense enzymes might be an important site of action for Irgarol 1051 and diuron in this cyanobacterium [100].

Glutathion-s-transferase catalyses the conjugation of the reduced form of glutathione (GSH) in response to pollutants in order to make the compounds more soluble [153]. This activity detoxifies endogenous compounds such as peroxidised lipids and enables the breakdown of xenobiotics. GSTs may also bind toxic substances and function as transport proteins [154]. Herbicide stress also influences the activity of GST in cyanobacteria which depends upon its nature and type of cyanobacteria.

Treatment with bentazon (0.75-2 mM) for 72 h significantly increased GST activity by 25-296% in Anabaena cylindrica [151]. In another study, however, molinate (0.75-2.0 mM) decreased the
activity of GST in a time and concentration dependent manner in *Nostoc muscorum* [124]. Wild strain of *Synechococcus elongatus* PCC 7942 exhibited time dependent inactivation of GST in presence of bromoxynil (30 µM). The response of mutant strain on the other hand, was different with the addition of bromoxynil (150 µM) which exhibited significant increase (65-80%) in the activity of GST [92]. Agrawal et al. [86] reported that treatment with butachlor at LC50 appreciably increased the GST activity in three species of cyanobacterium *Anabaena*, being maximum in *Anabaena* LC31 (2.49 fold) followed by *Anabaena* 7120 (2.1 fold) and *A. dolioiulum* (1.92 fold).

### 6.2 Non-enzymatic Antioxidant System

A number of low molecular weight compounds such as reduced glutathione (GSH), proline, ascorbate, tocopherol and carotenoids are reported to play key role to counter abiotic stress caused by pollutants in plants [123,155]. The primary function of GSH appears to be in the maintenance of intracellular redox homeostasis by affording protection against ROS [156,157]. The effect of abiotic stresses on GSH concentration in cyanobacteria is controversial as some researchers reported an increase in GSH with increasing stress while, others reported a decrease in GSH [158,159]. Bhunia et al. [158] reported that total glutathione (GSH and GSSG) level was reduced in a dose-dependent manner in *Nostoc muscorum* when exposed to the carbamate herbicide benthiocarb. GSH (14-66%) and GSSG (20-54%) levels significantly decreased in time- and concentration dependent manner in a 72 h experiment of bentazon (0.75-2 mM) exposure to *Anabaena cylindrica* [151]. In another study, the same authors have reported a decrease in GSH and GSSG content in *Nostoc muscorum* with treatment of 0.75-2 mM molinate [124]. Cellular GSH content of *Synechocystis* sp PUPCCC 64 was significantly less under stress of 10 and 20 ppm anilofos [43]. Kumari et al. [83] demonstrated a decrease in the total GSH content in *Aulosira fertilissima* with 65 µM butachlor treatment. Since chloroacetanilides are known to react with sulphhydryl group [160] and metachlor (analogue of butachlor) covalently modifies the cysteine residue in vitro [161], therefore, butachlor might react with thiol and glutathione, thereby reducing their contents. The cellular levels of GSH significantly increased in response to treatment with bromoxynil whereas GSSG level reduced in both wild and mutant strains of *Synechococcus elongatus* PCC 7942 [92]. Butachlor at LC50 dose registered a slight increase in total glutathione content in *Anabaena* LC31 (2.7 fold) than in *Anabaena* 7120 (2.5 fold) and *Anabaena dolioiulum* (2.48) [86].

Accumulation of proline has been reported to be an important biomarker of tolerance capacity in plants, bacteria, protozoa, algae, marine invertebrates, and also in cyanobacteria, due to its function as a stabilizer, a metal chelator, an inhibitor of lipid peroxidation, and a scavenger of singlet oxygen and hydroxyl radicals [162 and 163]. Paraquat at concentration ranging from 1-20 x 10−7 M increased proline content by 136-605% in *Anabaena variabilis* and by 105-297% in *Plctonema boryanum* indicating its involvement in detoxification of free radicals [48]. Proline content increased significantly in a time- and dose-dependent manner under bentazon (0.75-2.0 mM) stress conditions in *Anabaena cylindrica*. After 72 h, proline content was higher than control by 31, 166, and 655% in 0.75, 1.5, and 2 mM of bentazon concentration, respectively [151]. Oxyflurafen (10 and 20 ppm) and UV-B individually showed accumulation of proline in *Nostoc muscorum* while in combination of these stresses, proline content decreased indicating severity of toxicity. In contrast to this, proline showed continuous increase in *Phormidium foveolarum* under oxyflurafen and UV-B treatments suggesting its protective role during stress [97]. Molinate (0.75-2.0 mM) treatment significantly increased endogenous level of proline by 45-156% above control in *Nostoc muscorum* [124]. Anilofos (10-20 ppm) stimulated the synthesis of proline in *Oscillatoria simplicissima* in a dose dependent manner and maximum increase (369%) was reported in highest tested dose (20 ppm) of herbicide [41]. Significant enhancement of proline content (1.6 fold over control) by anilofos in *Anabaena torulosa* and *Synechocystis* sp. PUPCCC 64 has also reported [42,43].

Ascorbate functions as a source of reductant for many reactive oxygen species, thereby minimizing the damage caused by pollutant stress. Ascorbate scavenges not only H2O2 but also other free radicals such as O2·− and OH` and lipid hydroperoxide without enzyme catalysis [164]. Only few reports on the role of ascorbate in mitigating the herbicide stress in cyanobacteria are available. Cellular ascorbate content was affected by anilofos in dose dependent manner in *Oscillatoria simplicissima*. Maximum decrease (85%) was reported in 20 ppm of anilofos [41]. In
another study, herbicide anilofos (1.25-5.0 ppm) significantly decreased the ascorbate content by 60-75% in *Anabaena torulosa* [42].

### 7. BIODEGRADATION OF HERBICIDES

Cyanobacteria have been fully exploited for biological treatment of polluted waters, but only little information is available on how cyanobacteria participates in the process of biodegradation of chemical pollutants. It has been suggested that wild type cells of *Synechocystis* sp. PCC 6803 contain nitroreductase like DrgA protein encoded by Drg A gene which is involved in detoxification of herbicide dinoseb via the reduction of the nitro group(s) and this process is accompanied by the formation of toxic superoxide anions [165].

Cyanobacteria *Anabaena variabilis* and *Synechocystis* 6803 take up intracellularly different formulations of glyphosate when supplied in growth medium in the concentration range of 5-20 mM. The rate of uptake of herbicide was highest for roundup and lowest for free acids [59]. Ravi and Balakumar [166] reported that extracellular phosphatases produced by *Anabaena variabilis* were able to hydrolyze the C-P bond of glyphosate. With regard to degradation of herbicide in aqueous medium, Lipok et al. [167] concluded that mixed culture of *Spirulina* spp. exhibited a remarkable ability to degrade glyphosate. The rate of glyphosate biodegradation in the medium was independent of its initial concentration. They further suggested that glyphosate degradation pathway in *Spirulina* might be different from those exhibited in other bacteria. According to them, occurrence of herbicide metabolism in this cyanobacterium is evident, as the species was able to grow in a medium supplemented with phosphonate herbicide as the only source of phosphorus, where the rate of herbicide transformation was found to be depended upon the cells phosphorus status. Lipok et al. [168] reconfirmed the ability of the *S. platensis* to catalyze glyphosate metabolism. Four cyanobacterial strains (*Anabaena* sp., *Leptolyngbya boryana*, *Microcystis aeruginosa* and *Nostoc punctiforme*), out of the six strains studied by Forlani et al. [60], were able to use the glyphosate as the only source of phosphorus. Dyhrman et al. [169] reported the existence of phosphorous dependent glyphosate transformation in marine cyanobacterium *Trichodesmium erythraeum*.

The cyanobacterium *Anabaena inaequalis* metabolized isoproturon (3-(4-isopropyl phenyl)-1,1- dimethyl urea). The rate of degradation of isoproturon was 25% faster at pH 5.5 than at pH 7.5 when measured in ten day old culture. This was confirmed by using 14C labelled isoproturon and its metabolites accumulated in cells. Four detectable metabolic products such as monodesmethyl-IPU, OH-monodesmethyl-IPU, Didesmethyl-IPU and iso-propylaniline of isoproturon have been identified in this cyanobacterium [170].

Mansy and Bestawy [109] studied the biodegradation potential of fluometuron by six cyanobacterial species belonging to *Microcystis aeruginosa* (three strains), *Anabaena cylindrica*, *Anabaena flosaquae* and *Anabaena spiroides*. Exposure of these cyanobacterial strains to different concentrations of fluometuron (0.14, 0.7 and 1.4 ppm) at different exposure times (1-5 day) showed that biodegradation of herbicide was species specific and primarily correlated with exposure time reaching maximum efficiency after 5 days. Efficiency of these strains to biodegrade fluometuron was in the range 39-100%. Grötzschel et al. [171] studied biodegradation of 2,4 D by hypersaline cyanobacterial dominated mat collected from Guerrero Negro, Mexico under both photoautotrophic and heterotrophic conditions. Within 13 days, light/dark incubated mats degraded 97% of the herbicide in light where as in permanent darkness only 13% herbicide was degraded. Another cyanobacterium *Anabaena fertilissima* was also reported to biodegrade this herbicide. The exposure of cyanobacterium to 60 ppm of 2,4 D produced butyl ester after 4 days while isobutyril acid, allyl ester and 3-bromobutyric acid were recorded after 60 days. The exposure of this cyanobacterium to 80 ppm 2,4 D for 4 days yielded hydroxyl urea and trifluoroacetic acid, 2-methyl propyl ester. Acetic acid 2-propenyl ester, another product of 2,4 D was observed after 16 days of treatment. Another cyanobacterium *Westiellopsis prolifica* produced 2,4 D methyl ester and acetic acid after 4 and 16 days of exposure to 120 ppm of 2,4 D, respectively [172].

Commerially available mixed culture of *Spirulina* spp. exhibited a remarkable ability to biodegrade the widely used herbicide glyphosate that served as a sole source of either phosphorus or nitrogen. Phosphorus starvation of cells influenced the rate of glyphosate degradation. Further, the occurrence of additional peaks in NMR spectra which did not overlap with those of...
the most common intermediate of glyphosate degradation suggested that the cyanobacterium might degrade herbicide through a pathway different from previously elucidated in bacteria [168]. Forlani et al. [60] evaluated the ability of six strains of cyanobacteria to use glyphosate as a source of phosphorus when incorporated in growth medium in the absence of phosphate source. Of these, four cyanobacteria Arthrospira fusiformis, Leptolyngbya boryana, Nostoc punctiforme and Spirulina platensis were able to grow in presence of glyphosate indicating use of herbicide as a source of phosphorus.

The cyanobacterium Synechococcus elongatus takes up triazine herbicides atrazine and terbutryn (0.025-0.75 µM) intracellularly from the growth medium. The maximum uptake (50%) of these herbicides was observed at 12 and 6 h for atrazine and terbutryn, respectively. Data on herbicides bioaccumulation revealed that the limit value of accumulated herbicide after 12 h was 9 µmol g\(^{-1}\) dry biomass for atrazine and 12 µmol g\(^{-1}\) dry biomass for terbutryn after 18 h of incubation [173]. Another cyanobacterium Microcystis novacekii grown in medium containing 50-500 ppb atrazine removed 27% atrazine after 96 h. Spontaneous degradation was found to be less than 9% at 500 ppb concentration indicating a high efficiency for bioaccumulation of atrazine by the test organism. No metabolite was detected in the culture medium at any of the doses studied [57].

Biodegradation of acetachlor by cyanobacterial mat collected from Wadi Gaza near mediterranean sea was studied by El-Nahhal et al. [174]. Acetachlor (0.2-1.0 mg/kg soil) was added to soil and water samples pre-inoculated with cyanobacterial mat were inoculated. Results showed that acetachlor was degraded in both soil and water system with much faster rate in later system. Acetachlor concentration above field rate did not affect the biodegradation process in the water whereas it did in soil. Furthermore, bioremediation in water system was nearly completed in 15 days of treatment but did not reach high percentage of degradation in soil system.

The cyanobacterium Synechocystis sp. strain PUPCCC 64 was able to take up anilofos (10 ppm) intracellularly and metabolized it. The uptake of herbicide by the microorganism was fast in the initial six hours followed by slow uptake until 120 hours. The organism exhibited maximum anilofos removal at 100 mg protein\(^{-1}\) biomass, pH 8.0 and 30°C. The growth of cyanobacterium in phosphate deficient basal medium supplemented with 2.5 ppm anilofos indicated that herbicide was used by the strain PUPCCC 64 as a source of phosphorus [43].

Crouzet et al. [175] developed a microcosm in laboratory containing soil cyanobacterial communities to study the dissipation of pure form of mesotrione and its formulation callisto. Application of mesotrione at the rate of field application (3.4 µg kg\(^{-1}\)) caused approximately 75% dissipation within 14 days of treatments both in pure and formulation form while application at 10 folds concentration to field dose application, only resulted in 49 and 38% dissipation of initial applied pure mesotrione and formulation, respectively. The cyanobacterial communities in microcosm were able to remove 20% herbicide from 100 fold concentration to field dose. The nitrogen fixing cyanobacterium Nostoc muscorum took up butachlor intracellularly from medium. The GC-MS analysis of cell extract made from butachlor treated cells after 72 h treatment indicated the presence of 1, 2- benzenedicarboxylic acid and phenol as major biodegradation products [85].

Safi et al. [176] investigated the bioremediation of diuron in soil environment by cyanobacterial mats collected from agricultural fields of Gaza, Palestine. Diuron (0.055-0.88 ppm) was injected in water saturated soil samples pre-treated with cyanobacterial mat for several times. Growth of Jews mallow as a test plant was taken as indicator of biodegradation of Diuron. Results revealed that diuron was degraded in soil and degradation was more pronounced when diuron was incubated with cyanobacterial in the irrigation water. These encouraging results suggest that application of cyanobacterial mats could be a suitable method to remediate soil pollution. Sorption of herbicides, Paraquat and 2, 4-D by Oscillatoria sp. dominated cyanobacterial mat was studied as a function of pH, temperature and biomass. Mat biomass was an effective sorbent for paraquat but not for 2, 4 D. Increase in temperature also increased sorption of paraquat while 2,4 D showed opposite trend [177].

8. FUTURE PROSPECTS

- Although effect of herbicides on toxicity, photo pigments and photosynthesis of cyanobacteria are well documented in literature, interaction of herbicides on
enzymes of these physiological processes needs further attention.

- It would be interesting to know the detailed mechanism of degradation of herbicides by cyanobacterial enzymes or genes(s) involved.
- Cyanobacterial biosensors are not popular as compared to bacterial biosensors and thus there is plenty of scope for future research and development in this field.

9. CONCLUSION

The toxic effect of herbicides on photosynthetic pigments, photosynthesis and nitrogen assimilation by cyanobacteria varied with the nature, class and mode of action of chemical(s) and type and nature of organisms. These microorganisms tolerated herbicides by stimulation of enzymatic and non enzymatic antioxidant system or they followed the route of herbicide biodegradation.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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