

4-бөлім  
**ӨСІМДІКТЕР ФИЗИОЛОГИЯСЫ  
ЖӘНЕ БИОХИМИЯСЫ**

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Раздел 4  
**ФИЗИОЛОГИЯ И БИОХИМИЯ  
РАСТЕНИЙ**

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Section 4  
**PLANTS PHYSIOLOGY  
AND BIOCHEMISTRY**

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## **EFFECT OF CHROMIUM AND OTHER HEAVY METALS ON MICROALGAE**

This article is devoted to the identification of physiological and biochemical features of the influence of chromium and heavy metals (HM) on microalgae. The chromium-accumulating ability of some microalgae and influence of HM on the physiological-biochemical parameters of microalgae in mono-culture and mixed cultures are shown. The allelopathic relationships of microalgae and their influence on the processes of chromium and HM absorption are considered. Microalgae *A. flos-aquae*, *A. arnoldii*, *N. linckia*, *C. paryethina* actively absorb chromium from the culture medium are shown. The greatest absorption of chromium and HM occurs in microalgae cultures with positive allelopathic interference: *A. flos-aquae*, *A. arnoldii*, *A. flos-aquae*, *N. linckia*. In this article discusses the results of experiments with test-objects of different trophic levels. The unicellular algae is the most sensitive group of organisms to potassium dichromate that is shown. Particularly emphasized is the chromium accumulating capacity of certain plant objects, including microalgae. In studies on the effects of harmful substances on aquatic organisms, potassium dichromate is used as a reference toxicant. Their brief characteristics, pathways and migration, including intracellular and extracellular detoxification of HM ions, are given. The results of investigations are that physiological and biochemical processes of microalgae in conditions of environmental contamination with chromium ions have a general biological significance and can be used for the study of phytoremediation, ecological physiology and biotechnology. The data obtained in the research can be used to develop methods for biological treatment of wastewater and closed water systems contaminated with chromium.

**Key words:** Heavy metals, phytoplankton, microalgae, *Phaeodactylum tricornutum*, *Mytilus galloprovincialis* L.

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### **Хром және ауыр металдардың микробалдырларға әсері**

Мақалада микробалдырлардың физиологиялық және биохимиялық ерекшеліктеріне хром – мен ауыр металдардың әсері қарастырылған. Хромның микробалдырларды жеке және аралас өсіру барысындағы физиология-биохимиялық көрсеткіштеріне әсері туралы зерттеулер көрсетілген. Микробалдырлардың аллелопатикалық қарым-қатынасы және олардың хром мен ауыр металдардың сіңіру жүйесіне ықпалы анықталған. Микробалдырлар *A. flos-aquae*, *A. arnoldii*, *N. linckia*, *C. paryethina* тіршілік ету ортасынан қарқынды түрде хромды сіңіреді. Микробалдырдың аллелопатикалық қарым-қатынасы оң ортада хром мен ауыр металдарды сіңіруі белсенді жүзеге асады: *A. flos-aquae*, *A. arnoldii*, *A. flos-aquae*, *N. linckia*. Мақалада зерттелген түрлі трофикалық деңгейдегі сынақ – объектілерінің салыстырмалы-токсикологиялық ақпараттары қарастырылған. Біржасушалы балдырлар бихромат калий әсеріне өте сезімтал болып келеді. Зиянды заттардың су ағзаларына әсерін зерттеу кезінде, бихромат калий токсиканты ретінде анықталды. Сондықтан, оларға қысқаша сипаттама, көшіп-қону жолдарына, жасушаішілік және жасушадан тыс детоксикациясына анықтама берілді. Қоршаған ортаның хром иондарымен ластану жағдайында микробалдырлардың физико-биохимиялық үдерістерін зерттеу нәтижелерінің жалпы

биологиялық маңыздылығы жоғары, сондықтан фиторемедиация, экологиялық физиология және биотехнология курстарына қолдануға ұсынылады. Алынған мәліметтер сарқынды суды, хроммен ластанған және жабық су қоймаларын тазарту үшін биологиялық тәсіл ретінде пайдалануға болады.

**Түйін сөздер:** Ауыр металдар, фитопланктон, микробалдырлар, *Phaeodactylum tricornutu*, *Mytilus galloprovincialis* L.

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### Влияние хрома и других тяжелых металлов на микроводоросли

Статья посвящена выявлению физиологических и биохимических особенностей действия хрома и тяжелых металлов на микроводоросли. Показана хром-аккумулирующая способность некоторых микроводорослей и влияние ТМ (тяжелые металлы) на физиолого-биохимические показатели микроводорослей в моно- и смешанных культурах. Рассматриваются аллопатические взаимоотношения микроводорослей и их влияние на процессы сорбции хрома и других ТМ. Наибольшее поглощение хрома и ТМ происходит в культурах микроводорослей с положительным аллопатическим взаимовлиянием: *A. flos-aquae*, *A. arnoldii*, *A. flos-aquae*, *N.linckia*. В статье обсуждаются результаты сравнительно-токсикологического эксперимента тест-объектов различного трофического уровня. Одноклеточные водоросли в целом – наиболее чувствительная к бихромату калия группа организмов. В исследованиях по влиянию вредных веществ на водные организмы бихромат калия используется в качестве эталонного токсиканта. Приводится их краткая характеристика, пути миграции, в том числе внутриклеточная и внеклеточная детоксикация ионов ТМ. Результаты исследований физиолого-биохимических процессов в клетке микроводорослей в условиях загрязнения среды ионами хрома имеют общебиологическое значение и могут быть использованы при разработке методов биологической очистки сточных вод и замкнутых водоемов, загрязненных хромом.

**Ключевые слова:** тяжелые металлы, фитопланктон, микроводоросли, *Phaeodactylum tricornutu*, *Mytilus galloprovincialis* L.

Algae are an exceptionally convenient model object for studying the general patterns of the influence of toxicants simultaneously at the cellular and population levels (Seregin I.V., 2011:600; Nalimova A.A., 2005: 259; Allagulova C.R., 1999: 24; Yernazarova G.I., 2006: 146).

Among the test objects of different trophic levels (*Phaeodactylum tricornutum* AS algae, *Euplotes patella lemani* Dragesco, the early naupliar stage and the coryza of *Artemia salina* L., and the fertilized eggs of the bivalves *Mytilus galloprovincialis* L.) in the comparatively toxicological experiment, the unicellular algae are the group of organisms that is most sensitive to potassium dichromate (Verma S.K., 1995: 614). In this regard, algae, as one of the main test objects, are included in methodological documents for estimating the toxicity of contaminated aquatic environments. In studies on the effects of harmful substances on aquatic organisms, potassium dichromate is used as a reference toxicant (Michra B.B., 1997: 392; Singh Y., 1994: 149).

In accordance with the degree of toxicity for the life of microalgae HM (heavy metals) can be arranged in the following order [10]:

Sb > Ag > Cu > Hg > Co > Ni > Pb >  
> Cr > V > Cd > Zn > Fe (Mn, U).

It should be noted that some light metals, such as aluminum, also exhibit toxicity. Phytoplankton organisms, to some extent, have the ability to withstand the toxic effect of HM.

In the review of A.V. Lebedeva, etc. (1998: 42) the concepts that characterize the varying degree of resistance of algae to the action of heavy metals are clearly defined. Here are explanations of some terms which will be used often in subsequent discussion.

The growth and development of microalgae in a certain range of HM concentrations, due to genetic characteristics, can be characterized as tolerant. The ability of microalgae populations to resist HM concentrations outside the tolerant zone is characterized as resistance. The concept of resistance is closely related to adaptation - the ability to experience unfavorable conditions that caused the death of a given organism and survive.

It has been established that laboratory cultures of green microalgae (*Scenedesmus sp.*, *Chlorella sp.*) are more resistant to chromium than diatomaceous algae cultures (*Fragillaria crotonensis*). In

natural populations of phytoplankton at elevated Chromium (Cr) concentrations, dominance of algae flora in some water systems changed from diatoms and blue-green to green algae (Purchase D., 1997: 85; Wakatsuki T.: 1996: 170). At the same time, the exceptional resistance of blue-green algae, which have gel-like mucous membranes on the cell surface, also performed the function of chelation with many elements (Popova V.V., 2000: 150).

The level of manifestation of the toxic effect of metals depends on their concentrations in the cell and the duration of action, as well as on abiotic factors (the composition of the medium, and the presence of other toxicants), and biotic factors (interaction with bacteria, algae and other hydrobionts, as well as the physiological state of the microalgae culture). The influence of external conditions on the resistance of cells to HM is, as a rule, mediated: changes that reduce the mobility of HM ions also reduce their accumulation (Stom S.J., 1995: 321). The presence other cations can also have the toxic effect of chromium. Thus, in the presence of Ni (Nickel), the sensitivity threshold of algae to chromium is significantly reduced. The resistance to  $\text{Cr}^{6+}$  of the culture of diatoms *Fragillaria crotonensis* changes practically at any variation in ambient conditions: changes in illumination, pH, composition of the medium, its chelating properties, etc. In natural phytoplankton populations, the maximum inhibition of growth is observed when Cr concentrations increase to 10 mg / L, and water temperature and illumination decrease. For most species at the beginning of the lag phase of the growth curve of culture, the sensitivity to the effect of HM is maximal, and at the end - minimal. In the stationary phase, the increase of cell resistance is associated with a general increase of the suspension density and the accumulation in the culture medium of exometabolites capable to bind metals [10]. The sensitivity of algae to the HM action depends on the seasonal influence, because their genetic mechanisms of control the activity of metabolic processes are closely associated with them. When studying the dynamics of changes in the individual and population characteristics of the culture green *Protococcal alga Scenedesmus quadricauda* in different seasons of the year, depending on the concentration of potassium dichromate in water, it was found that the highest level of plant resistance to toxicosis occurs in autumn (September-October). In winter (February) the culture shows minimal stability, and in summer (July) the level of stability is intermediate between the two above (Rai L.C., 1998: 321). The influence of biotic factors on the stability of microalgae to the chromium action

is due to the influence of the accompanying bacteria, as well as the interspecific interactions of various representatives of the algophlora. If the influence of concomitant bacteria in the metal absorption processes has been studied to some extent, and the influence of inter-species interrelations of microalgae on adaptation processes and toxic resistance has not been considered. In heterogeneous natural populations, the resistance to HM is largely determined by the groups of microorganisms that formed the population. It is believed that the intensive development of microalgae in the presence of sublethal concentrations of HM can be associated with a better supply of the population with organic and mineral resources by suppressing the development of concomitant bacterial flora. Bacterioplankton are less resistant to HM than phytoplankton. The effect of HM on the stability of microalgae and bacteria can be mediated - through the effect on chemical characteristics, oxidation-reduction potential, pH of the medium.

In laboratory and natural communities consisting of microalgae and bacteria, the autotrophic component releases organic substrates that support bacterial growth and promote the accumulation of ions and metal suspensions in the immediate environment of cells. Bacteria, in turn, provide oxidation, reduction and precipitation of bound HM in mud and "microbial films" (Visviki I., 1994: 155). Such communities can survive at high concentrations of dissolved metals and metalloids - Pb, Cd, Zn, Co, Cr, Mn, Se and As (Rijstenbiel J.W., 1994: 321). It is shown, for example, that the stability of the cyanobacterium *Nostoc muscorum* to  $\text{Cd}^{2+}$  up to  $10^{-4}$  M (growth inhibition of the cyanobacteria under investigation is observed at  $10^{-7}$ - $10^{-6}$  M) is ensured by the presence of accompanying bacteria in their casings effectively binding  $\text{Cd}^{2+}$  ions to CdS. The formation of CdS occurs as a result of the interaction of Cd with the released  $\text{H}_2\text{S}$ -satellite (Mangala G., 1995: 972).

Adaptation of algae to high concentrations, which can even cause cell death, is primarily due to functional changes. With a sharp increase in the concentration of toxicant in the environment, algae cells become stressed.

Strictly speaking, stress is not an absolutely steady state. If the effect of the factor is long, then the cell can either perish, or adapt to life under new conditions - go into homeostasis. Adaptive changes in the latter case are associated with the launch of gene-regulatory mechanisms, the inclusion or deactivation of the corresponding hereditary programs. The inclusion of repair mechanisms takes some

time, so stress, as a condition characterized by increased resistance, provides a temporary experience of the cell with an adverse moment (Sargent J.R., 1993: 460). It is believed that the rate of return of the biosystem to its original state can characterize its reliability (Sakamoto T., 1997: 100; Kaplan D., 1995: 129; Kosakowska A., 1996: 50).

On the example of the effect of potassium dichromate on green algae - *Scenedesmus* - the universal character of the dynamics of the toxic effect is shown (Suginta K., 1997: 69). A study was made of the development of toxic stress when a given toxicant was included in the medium in a wide range of concentrations, which included homeostasis (small doses), stress (medium doses), and pre-condition (large doses). In the early stages of the manifestation of the toxic effect for the development of culture, significant fluctuations in the total number of cells were characteristic, which in the physiological and toxicological literature are usually described as phases of oppression and stimulation (Monks T., 1994: 143). The fluctuations in the characteristics of the cultures in these experiments were due to a change in the rate of division and lysis of the cells. The authors consider the dynamics of the toxic effect as a result of the interaction of two simultaneously occurring processes - destruction (damage) and compensation-adaptation, or impulse and response. The first process is predominantly passive, the second is active. The beginning of the formation of the toxic effect is associated with a great variety of physiological and biochemical reactions taking place at this time, caused by the process of destruction of biological structures and functions. At this stage, the system of homeostasis of the organism, the violation of the permeability of cell membranes, the development of free radical reactions, etc., are unbalanced (Ahner B.A., 1995: 649; Agrawal S.W., 1993: 223). Along with the processes of deformation and destruction, after a certain time after reaching a certain threshold of damage, the mechanisms of repair, restoration of disturbed structures and functions are included. Thus, the dynamics of the toxic effect on the population of microalgae is the alternation of the phases of disturbance and restoration of the observed functions. Thus, in cultures of the stages of chromosomes under the influence of chromium, changes in cell size were noted. With the development of algae in a medium with dichromate concentrations of 1-3 mg / l, a positive correlation of the total number of cells and their absolute sizes was noted. At high concentrations of toxicants in the medium (6-10 mg / l), the number of cells decreases. Particularly significant reduction of the proportion

of living cells. With the appearance of a toxic effect, the relative dimensions of the strom cells increase, and the width changes more significantly. As a result, there was an increase in the surviving cells to a larger size than in normal, which precedes their division. Similar changes in cell size with inhibition of cell division under the action of heavy metals were observed earlier (Mamta A., 2004: 242). On the 33rd day of cultivation at a concentration of 10 mg / l dichromate, the total number of cells was only a tenth of the control, and the proportion of living cells did not exceed 3% of the control population. The decrease in the number of cells in the culture can be both the result of slowing down their growth and division, and the acceleration of death (Berry J.P., 1966: 401). Elimination of the weakly stable part of the population and the selection of ready-made resistant forms contribute to the adaptation to the action of toxic concentrations of HM. The subsequent resistance of the culture is determined by the appearance of progeny of resistant cells. Such a mechanism is characterized as a genotypic adaptation of a population based on changes in its gene pool. As one of the variants of genotypic adaptation, gametogenesis observed in *Scenedesmus* can be considered. Acutus with prolonged action of potassium dichromate (3 mg / l) and after its termination, because the sexual process leads to the exchange of genes between cells, which increases the probability of the formation of resistant forms. Such adaptation forms lines not only tolerant to the initial level of pollution, but also capable of transferring increasing concentrations of the toxicant. Acquired properties persist for a long time: resistance to Cr populations of *Sc. Quadricauda* and *Sc. Asutus*, exposed to potassium dichromate (1 mg / L) for 30 days, was preserved after several months of cultivation on a clean medium (Sausser K.R., 1993: 60).

Resistance to the influence of HM is determined by a complex of simultaneously acting and complementary mechanisms: a decrease in the accumulation of HM, a decrease in the permeability of cell membranes for metals; Removal of metals from cells and detoxification of metals in the medium, on the surface and inside cells. For each species, there is a certain limit, after which the HM entered into the body inhibit the life activity of microalgae, violate physiological processes, including mechanisms that regulate the metal content in cells. Further unregulated entry of HM can lead to cell death (Gusev M.V., 1997: 14). The mechanisms of the stability of algal cells can be conditionally divided into two groups: extracellular, associated with the prevention of metal penetration into the cell, and intracellular

ones, based on changes in the metabolism of cells into which metal ions penetrated and leading to its immobilization and detoxification. "Extracellular" mechanisms of stability are determined by high cationic capacity of cell walls, glue mucus, microalgae and cyanobacterial covers: toxic ions are immobilized before they enter the cell membrane (Surosz V., 2000: 224). The resistance to HM, correlated with the thickness of the cell wall, is observed in the mutant forms of *Chlorella sp.* Strains with an underdeveloped cell wall are much more sensitive to Zn, Cu, Pb and Cd than the wild type (Idris M., 1998: 80). The barrier function of the cell membrane, i.e. Of all surface layers located on the outside of the cytoplasmic membrane is associated with its significant volume (in the blue-green alga *Anabaena cylindrica* - up to 20-30% of the dry mass, including mucous surface layers similar in composition to the polysaccharide released by the cells into the medium, or more Complex multilayered fibrillar structures) and is due, on the one hand, to the ability of glycosaminoglycan to gel formation, on the other hand, to the degree of "cross-linking" of tetrapeptides. The outer layer can be enriched with calcium and silicon, which further increases the protective capabilities. The surface structures of the cells of the "old" cultures are more developed than the young ones (Karavayko G.I., 1997: 531). The total binding of *Chlorella sp* and *Spirulina maxima* cells to Co, Ni, Zn and Se ions is estimated at 20-35%. The leading role in binding is played by the polysaccharide component. Zn is bound by proteins from the outer layer of the *Synechocystis aquatilis* cell capsules (Lemenovskiy D.A., 1997: 52; Reunova Y.A., 2004: 116). Absorbed Cu, Fe, Ag, Au form aggregates in the cell wall of *Chlorella vulgaris* (Avery S.V., 1993: 812).

The ion-exchange properties of the cell wall polysaccharides determine not only the mitigation of the toxic effect of HM ions, but also the slower restoration of disturbed physiological processes. Cadmium ions on the surface of *Nostoc muscorum* cells are involved in the biosynthesis of CdS crystallites. The source of sulfur for this biosynthesis is the components of the mucosa (Sadhukhan P.C., 1997: 72). From bound particles less toxic than Cd<sup>2+</sup>, CdO and CdS, *N. muscorum* cyanobacteria are released by accelerated synthesis of mucous membranes. Reduction of the toxic effect of HM in the late stages of the development of the culture depends on their chelation by accumulating extracellular metabolites of algae. Cyanobacteria *N. muscorum* secrete up to 1 g of polysaccharide per 1 g of dry biomass; Total excretion of extracellular organic matter by phyto-

plankton is estimated at 7-50% of total fixed carbon, its origin is associated with cell multiplication, re-assimilation and autolysis processes (Li Y., 2004: 696). Exopolysaccharides protect cells from ions Cu, Pb, Cr.

The increased isolation of exometabolites is presumably induced by metal ions, which, penetrating the cell, affect its metabolism. Thus, when incubated with Cd, the content of *N. muscorum* exopolysaccharides increases, their kinetics and concentration depend on the Cd content in the medium, and the composition of monosaccharides changes. An increase in the synthesis of organic substances in the presence of HM is observed in many species of blue-green algae. The biofloculants they release are polyanionic compounds with a molecular weight of more than 200 kDa, including up to 2.2% galacturonic and up to 1.86% glucuronic acids (Rijstebiel J.W., 1994: 323). The composition of the extracellular flocculent *Anabaena sp.* (Strains No. 144 and PC-1) include neutral sugars, uric acids and proteins. The exometabolites of the cyanobacterium *Synechococcus sp.*, Released under the influence of toxic concentrations of Cu, reduce its concentration to sublethal.

In the cells of microalgae, the processes of the entry of metals from the solution and their elimination occur simultaneously. Adaptation of microalgae to the action of HM is associated with the establishment of a dynamic equilibrium between these processes. Resistance to HM often correlates with resistance to low pH, which is explained by the participation of general mechanisms: the development of hyperactivity of ATPase, changes in the overall membrane potential and membrane permeability.

Endogenous resistance to HM is provided by intracellular rearrangements and metabolic changes aimed at isolation or binding of the metal with subsequent excretion from the cell or localization in it (Allagulova CH.R., 1999: 24). This also includes mechanisms that ensure the neutralization of toxic effects of metals: DNA repair, proteolysis of damaged proteins, metabolism of products of lipid peroxidation and the destruction of damaged lipids from membranes.

Maintaining homeostasis and increasing metabolic processes in cells to accelerate the elimination of toxic substances are accompanied by an increase in the costs of ATP and depletion of the energy resources of the cell. In the first hours of exposure to Cu, Fe, Ag, and Au on *C. vulgaris*, *N. muscorum* and *Dunaliella salina* cells, activation of photosynthetic and respiratory intensity associated with detoxification processes was observed (Avery S.V.,

1993: 815). Toxic effect of HM decreases with the presence of intracellular reserves (energy reserves of lipids, carbohydrates), with round-the-clock illumination of microalgae or in the presence of an energy substrate. Least resistant to HM culture of physiologically young cells, depleted in minimal media. As one of the mechanisms of physiological adaptation is the hyperaccumulation of HM ions and their recovery within cells. Hyperaccumulation in cells of a number of heavy metals is carried out with the participation of biopolymers (ligands) or metal oxidoreductases (hydrogenases). Internal structures of *Chlamydomonas reinhardtii* and *Sc. Aqutus* bind up to 50% of absorbed  $Hg^{2+}$ , Cu, Cd, U, Pb, Zn and Ni (Surosz V., 2000: 198). Up to 40% of the absorbed Se form intracellular complexes with proteins and lipids in the cells of the green microalga *Chlorella sp.* And cyanobacteria *Spirulina subsalsa*, *S. maxima* and *S. platensis*, with proteins accounting for 14.6% of the absorbed Se, and lipids - 16.05% (of which 2/3 - polar) (Lemenovskiy D.A., 1997: 49; Reunova Y.A., 2004: 116). Under the influence of Hg in the cells of *Nostoc*, *Aphanothece*, *Cylindrospermum* and *Gloeotrichia*, the content of free amino acids, nucleic acids and proteins decreases. Co<sup>2+</sup> resistant strain *Spirulina platensis* is characterized by more efficient binding of the toxic ion by intracellular structures than sensitive. The protective role of low-molecular metabolite cells can be in this case associated with the formation of safe complexes with HM ions or with an impediment to the binding of HM to biomolecules. In the cells of *Chlamydomonas reinhardtii*, *Dunaliella salina* and *Chl. Bullosa* treaH-Ment of Co, Cu or Cd leads to the accumulation of starch [32]. Intracellular polysaccharides are associated with such HMs as Cu, Fe, Mg, Zn, Pb, Hg, Cd and others [33]. With intracellular reduction of HM ions, the soluble toxic compound becomes inaccessible. In the recovery of HM ions, electron transfer systems contained in the cytoplasmic membrane (in eukaryotic cells - and mitochondrial systems) participate. In *S. platensis* cells, a part of the absorbed selenite is reduced to elemental Se. In blue-green alga *A. variabilis*, resistant to low concentrations of  $Cr^{6+}$ , the ability to restore it to  $Cr^{3+}$  is widespread among facultatively anaerobic bacteria. According to the mechanism of toxic effect, HM ions can be divided into two groups: the first (Fe, V, Cu, Cr, etc.) in the cells undergo redox cyclization, and the second (Cd, Hg, Ni and Pb, etc.) The exhaustion of the reduced form of glutathione and protein SH-groups, which leads to the accumulation of peroxide ions, hydroxyl radicals and  $H_2O_2$ . In both cases, inhibition of the activity of certain enzymes and an increase in per-

oxidase activity and lipid peroxidation are observed. The formation of peroxides, in turn, leads to DNA ruptures and the release of  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  ions from the cells as a result of damages to the plasma and vacuolar membranes. These disorders help inhibit the biosynthesis of chlorophyll, photosynthetic and respiratory activity, cause destruction of chloroplasts and mitochondria (Gusev M.V., 1997: 14).

In addition to homeostasis and reactive metabolite  $O_2$  in the inactivation of HM from the first group (Cu, Co, Cr), antioxidants also participate. Reduction of resistance to Cu and Co *Anabaena doliolum* and *Chlorella vulgaris*, observed under the influence of ultraviolet radiation, is associated with increased oxidation of membrane lipids and a change in the conformation of enzymes. Diatom alga *Ditylum brighfwellii* under the influence of Cu (3-126 nM) increases the activity of peroxide dismutase. In *C. vulgaris* cells, the activity of superoxide dismutase and catalase increases by 40-500%, the content of tocopherol and  $\beta$ -carotene by 60-180% (Rijstebiel J.W., 1994: 389). Among the low molecular weight antioxidants involved in protecting against oxidative stress include some lipids of diatoms, dinoflagellate, *Prymnesiophyta*, coccolithophoride, vitamins B<sub>2</sub>, E and C, phenolic components, carotenoids (most known antioxidants), glutathione and some other exo- and endogenous thiols. Membrane-bound tocopherol (vitamin E) converts free radicals into a stable form and promotes their removal from the membranes. With a low level of cellular tocopherol, the protective effect of exogenous thiols also decreases (Sargent J.R., 1993: 460).

Resistance to the toxic effect of HM belonging to the second group is determined by their interaction with SH-groups and the ability of cells to produce thiol compounds. Thiol compounds: cysteine, thioglycolic acid and glutathione - contribute to reducing the effects of Cd on *Chlorella sp.* and Co on *Sc. Armatus* and *Synechocystis aquatilis*. It is shown that the main low molecular weight thiol in protecting a plant cell from stress is glutathione: it participates in the reactions of antioxidant enzymes, cells with a high content of glutathione are more resistant to oxidative stress. The accumulation of glutathione in cyanobacterial cells is promoted by cysteine and some other sulfur compounds contained in the medium. Depending on whether the synthesis of compounds that bind HM is inducible or whether they are formed in the cell independently, one can speak of specific or nonspecific binding. Conjugates formed during nonspecific binding of HM glutathione and other low-molecular metabolites are often more toxic than the initial ions, and the reversibil-

ity of binding of glutathione conjugates leads to the fact that they serve as a transport form for reactive metabolites that are released in the “target organs”. The toxic effect of the conjugates can be direct-via covalent binding-or indirectly-through oxidation of bases, inhibition of enzymes in which glutathione is a cofactor. The non-specific binding or oxidation of glutathione with HM ions leads to a separation of the processes of biosynthesis and cell division and an increase in their size. An increase in cell size was observed, in particular, in *Scenedesmus quadricauda* and *Sc. Acutus* under the action of Cr ions. The compounds providing the specific stability of microalgae and cyanobacteria to HM include metallothioneins (MT), their plant analogs of phytohelatina (PC) and low-molecular (g-glu-Cys) peptides (Maywald F., 1997: 121). Glutathione is their predecessor. Thus, the synthesis of metal-binding peptides by  $HgCl_2$  in the cells of the green alga *Cosmarium conspersum* correlates with an increase in the total content of glutathione, while the amount of its reduced form (GSH) decreases and increases with the oxidized (GS-SG). This group of proteins is characterized by a molecular weight of up to 10 kD and a high content of thiol groups. Adjacent cysteine residues in the molecule allow HM to bind up to 7 divalent (or up to 12 monovalent) HM ions. It is shown that when the intracellular content of Cu and Cd is increased, the growth of cultures of green microalgae *Scenedesmus sp.*, *Chlorella sp.*, *Diatom alga Phaeodactylum tricornutum* is accompanied by active synthesis of PX, and the use of inhibitors of PX synthesis causes a decrease in cell resistance to HM. MT, PC and the HM ions (Cu, Cd, Fe, Mn, Zn) associated with them are usually localized in the cytoplasm and vacuoles. In the cells of *Chlamydomonas reinhardtii* and a number of other unicellular green algae, there is a strong vacuolization of the cytoplasm and the appearance of dense inclusions in vacuoles. In the cytoplasm or lysosomes, the associated Ni, Cu, and Ag ions accumulate in the form of sulfur-containing compounds, and Al and Cr are predominantly in the form of insoluble phosphorus-containing compounds. In the cytoplasm and carboxysomes of the green alga *Plectonema boryanum* Zn, Pb, Mn and Al are concentrated in granules of polyphosphate. The removal of bound HM ions can occur both by exchange for free ions in the cytoplasm and with the liberation of the metal complex with degradation products of MT, as shown for diatoms and blue-green algae (Rijstenbiel J.W., 1994: 391). Metal chelating, storage and transport proteins also participate in the chelation of HM in cells (Maywald F., 1997: 111). In cells *Phormidium*

*sp.* In the presence of Cu, an increase in the amount of cyanophilic granules is observed. In proteins of the blue-green algae *Spirulina subsalsa*, *S. maxima* and *S. platensis*, 14.6% of the absorbed Se bind, of which 59% are associated with the proteins of the chlorophyll-protein complex (Lemenovskiy D.A., 1997: 51). When Cd (0.5-1  $\mu g / ml$ ) was incubated in *Anabaena flos-aquae* cells, a Cd-binding protein with a molecular mass of 25-26 kDa was observed, Sn (5-10  $\mu g / ml$ ) formed Sn-binding A protein with a molecular weight of up to 70 kDa, bound to soluble pigments. It is known that the stability of *Pseudomonas sp.* To the cations of Hg, Cd, Cu, As and Cr anions is encoded in the chromosome and plasmids. Apparently, like bacteria, the resistance of cyanoprokaryotes to HM can be encoded at the level of chromosomes, plasmids or transposons with the participation of one or more genes. Thus, Cd directly affects the transcription of DNA, affecting the synthesis of HM and stress proteins. At the biochemical level, there are up to six main mechanisms of resistance to HM. The main mechanism of resistance to Hg is the redox transformation, encoded by the wer operon. Resistance to single metals is often independent of resistance to others. For example, the Cr-tolerant strain *Scenedesmus acutus* is much more resistant to the wild to the action of Cu, while the resistance to Zn is independent of the resistance to Cr (Wakatsuki T., 1996: 173).

It is believed that the mechanisms of resistance to metals necessary for a cell must be inducible, since constitutive expression can deprive cells of the necessary metals at low levels in the medium.

The effect of chromium is reflected in the level of viability of all crops, causing a significant decrease in it. Thus, in monocultures at a concentration of 0.2 mg / ml only 7-10% of cells remain alive. In mixed cultures with negative allelopathy, there is a significant decrease in the viability of cells of the suppressed species until complete disappearance. Thus, at a chromium concentration of 0.2 mg / ml in a mixed culture of *A. flos-aquae* x *C. parietina*, no living cells of the calotriks were detected, while the anabene is more viable (by 8%). In mixed cultures with positive allelopathy the damaging effect of chromium is less noticeable than in monocultures and mixtures with negative allelopathy. In variants with a concentration of 0.2 mg / ml of chromium, the viability level of cells of both species is several times higher than in monocultures (Dzhokebaeva S.A., 2012: 11).

To sum up the phytoplankton organisms, being the primary producers, are those components of water systems on which the toxic effect of HM primar-



ily affects. Their own stability can adversely affect the general state of the ecosystem in connection with the possibility of accumulating HM and transferring them through food chains. As a rule, metals associated with organic compounds, including microalgae exometabolites, are less mobile and, in most cases, less toxic and less accumulated by cells of living organisms and easier to sediment, accumulating in mud and microbial films. The organic forms of mercury (methyl- and dimethyl-mercury) or tin are much more toxic than the initial ions, but they are

more assimilated than the mineral blue-green *Synechocystis* PCC-6803, *Plectonema boryanum* and the green alga *Chlorella*. As the molecular weight of the compound increases, so does the activity of accumulation (Lebedeva A.F., 1998: 46). The HM ions bound by organic compounds of cells are not permanently derived from the cycle of biogenic elements. Organometallic compounds, in turn, undergo microbial degradation, in which free metals are released into the medium. Both these processes play an important role in the cycle of metals in nature.

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