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THE ROLE OF CHELATE COORDINATION COMPOUNDS OF BIOGENIC METALS IN THE VITAL ACTIVITY OF PLANTS.

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The review article discusses the main issues of creating and using modern chelated microfertilizers based on trace elements in agricultural production. Issues of the role of microelements in the vital activity of living organisms and methods of overcoming the lack of microelements in plants are highlighted. An overview of coordination compounds of 3d-metals (Fe, Mn, Zn, Cu, Co, Ni, Mo) with different classes of complexons, features of their structure and properties is presented. It contains relevant material on the use of microelement complexes for the creation of modern chelated fertilizers. Attention is paid to the use of trace elements complexonates in areas contaminated with radionuclides (^{137}Cs, ^{90}Sr).

Keywords: coordination compounds, microelements, chelates, complexones, fertilizers, plants.

INTRODUCTION. It is possible to eliminate pathological phenomena caused by a decrease in the level of biometals in plants by introducing trace element additives into the soil in a form that is easily transported and assimilated by living organisms. In recent years, the interest of scientists in the creation of effective and environmentally safe growth regulators has increased: the development of methods of their synthesis, the mechanisms of action and methods of application are being studied.

The role of microelements (ME) in the life activity of living organisms is well known. Pathology associated with the lack of ions such as iron, zinc, manganese, copper, cobalt, zinc leads to various functional diseases, impaired metabolism, possibly to the death of animals, reducing productivity and crop yields [1–6]. Microelements are involved in such important biochemical processes as respiration, photosynthesis, protein synthesis, blood formation, protein, carbohydrate and fat metabolism, humus synthesis. Due to their catalytic action, microelements allow plants to more effectively use the main nutrients – solar energy, water and macroelements - nitrogen (N), phosphorus (P)

and potassium (K), which, in turn, has a positive effect on plant productivity and harvest quality. Microelements are able to strengthen the ability of plant tissues to recover, which significantly reduces damage to plants by diseases. Most trace elements are active catalysts of biochemical processes in plants. In addition, trace elements affect the direction of biochemical reactions in plants due to their influence on plant biocolloids. Microelements cannot be replaced by other substances and their deficiency must be filled taking into account the form in which they will be in the soil. Plants can use trace elements only in water-soluble form (mobile form of trace element), and the immobile form can be used by the plant after complex biochemical processes involving soil humic acids.

The main role of trace elements in increasing the quality and quantity of the crop is as follows:

1. In the presence of the required amount of trace elements, plants have the ability to synthesize a full range of enzymes, which will allow more intensive use of energy, water and nutrition (N, P, K) and, accordingly, to obtain a higher yield.

2. Microelements and enzymes based on them strengthen the regenerative activity of tissues and prevent plant diseases.

3. Microelements are one of the few substances that increase plant immunity. Their lack creates a state of physiological depression and general susceptibility of plants to parasitic diseases.

That is why today there is a need to create and use new environmentally friendly effective trace element compounds, both in plant and animal production, which are lacking in soils and rations, in order to increase plant yields, improve animal productivity and the quality of plant products . Therefore, the creation of new non-toxic and effective drugs that contribute to the successful resolution of urgent issues in some sectors of agriculture is an important task for agro-industrial complexes around the world.

BIOLOGICAL ROLE OF METALS. The most important microelements in plant life are iron, copper, zinc, manganese, magnesium, cobalt, molybdenum, which, according to their importance in living organisms, can be placed in the order Fe>Mn>Zn>Cu>Co>Ni>Cr>V>Mo. Boron, magnesium, calcium are classified as mesoelements, since for the life activity of plants, they are required in much more amounts than microelements.

The physiological significance of the main trace elements for plants is given in Table 1.

Iron plays a leading role among all metals contained in plants. Organic compounds, which include iron, are necessary in biochemical processes that occur during respiration and photosynthesis, which is explained by a very high degree of their catalytic properties. The catalytic effect of iron is related to its ability to change the degree of oxidation. The iron ion is oxidized and reduced relatively easily, therefore iron compounds are carriers of electrons in biochemical processes. The process of electron transfer is the basis of the reactions that occur during plant respiration. This process is carried out by enzymes – dehydrogenases and cytochromes containing iron. Among other processes, the influence on the formation of the structure and functioning of chloroplasts, as well as the synthesis of chlorophyll, should also be noted [7].

Table 1.

Physiological significance of the main microelements in plants.

ME	Functions in plants	Symptoms of deficiency and its consequences	Plants prone to deficiency
Fe	• A necessary component of many enzymes in plants. • Is contained in chloroplasts and takes part in the photosynthesis and metabolism of N and S. • The main component in the synthesis of chlorophyll.	• Can stimulate chlorosis, which appears on young leaves due to low mobility of Fe in the plant. • In cereals, chlorosis manifests itself in the form of interspersed yellow and green stripes along the leaf. • Fe deficiency often causes shoot dieback.	Citrus, fruit trees, vineyards, legumes, corn, tomatoes, roses and ornamental plants
Mn	• necessary for normal photosynthesis, • participates in the reduction of CO_2, • plays a role in maintaining the structure of chloroplasts. • participates in the synthesis of vitamin C	• Violation of the ratio of elements of natural nutrition, • occurrence of point chlorosis, • sometimes complete absence of fruiting	Oats, barley, beets, beans, tomatoes, apple trees, roses
Zn	• Catalyst in many enzyme systems. • As part of enzymes, it participates in the metabolism of starch and nitrogen. • Metabolism of carbohydrates, phosphates and proteins; formation of growth hormones auxins, DNA, ribosomes.	• growth retardation - shredding • short internodes • interveinal chlorosis • brown spots on upper leaves • deformed leaves and fruits	Corn, hops, beans, flax, green vegetables, citrus fruits, grapes, apples and pears
Cu	• Mainly in the composition of proteins in green cells, responsible for binding solar energy. • Along with Zn, activates an enzyme that prevents the destruction of plant cells. • Participates in the process of protein and carbohydrate metabolism	• Chlorosis and curling of leaves due to dying of their tips. • Weakened ovary in cereals - drop in yield in the absence of visible signs of deficiency. • Reduced release of pollen grains, which leads to less pollination of flowers and reduced yield. It causes "hanging" of tree crown branches and laying of cereals (low yield).	Cereals, citrus fruits, apple trees, pears, green vegetables, rice, alfalfa.
Co	•A component of vitamin B12, necessary for nitrogen fixation in plants • increases the intensity of respiration and photosynthesis, contributing to the formation of chlorophyll and reducing its decay in the dark	• Poor growth can be corrected by using ammonium and nitrate nitrogen. • Manifestation of chlorosis on the leaves. • Slow plant growth • Development cycle lags behind the norm.	Beans, peas, clover, alfalfa
Mo	•Provides plants with nitrogen • participates in hydrocarbon exchange, in the exchange of phosphorus fertilizers, in the synthesis of vitamins and chlorophyll, • affects the intensity of redox reactions	• the edges of the leaves acquire an orange, red or pink shade • Plant growth is inhibited, leaves are deformed and die prematurely. • nitrates accumulate and nitrogen metabolism is disturbed - the content of ascorbic acid decreases. • violations of the phosphorus metabolism of plants are observed.	soybeans, grain and leguminous crops, clover, perennial grasses

To activate the process of iron up take by the plant, a biochemical adaptation of the primary metabolism is necessary, which requires primarily changes in energy consumption in the form of macroergic compounds, which are represented in the cell by such basic forms as nicotinamate (NADadenine) dinucleotide phosphate and adenosine triphosphate. In the course of the development of any organism, the most important role in providing cells with these components belongs to mitochondria, since for adaptive reactions, the effect of iron deficiency on these qi organelles is important [8].

A high degree of mitochondrial sensitivity in this aspect can be explained by the high need for iron to maintain the activity of metalloenzymes, iron-sulfur proteins and cytochromes, thanks to the work of which protons and electrons, ultimately, are transferred to the oxygen in the air. Electron carrier proteins include iron-sulfur proteins (Fig. 1), containing fragments of the (Fe-S)n ferredoxin cluster. In them, iron is tetrahedrally surrounded by sulfur atoms of thiolate fragments of cysteine. In addition to cubic clusters of the type [4Fe - 4S], larger ones are also known: [8Fe – 7S] and [Mo-7Fe-8S-X] (in nitrogenase).

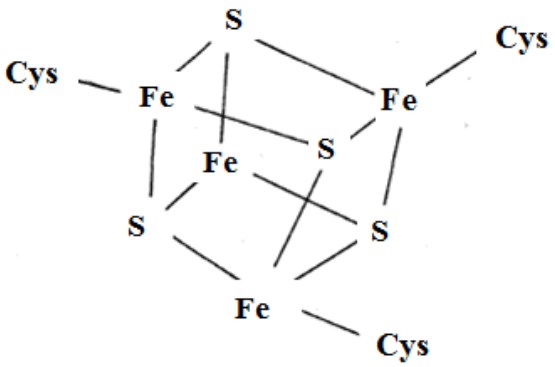


Fig. 1. – A fragment of the iron-sulfur protein structure (Cys is a cytein residue).

Iron is necessary for the synthesis of cytochromes, pyridoxine and other iron-sulfur proteins, components of the reaction centers of the chloroplast photosystem, cytochrome oxidase, catalase, peroxidase and other enzymes that play key roles in the main physiological processes – photosynthesis, respiration, nitrogen fixation and metabolism.

Iron has a special function – indispensable participation in the biosynthesis of chlorophyll. Therefore, any reason that limits the availability of iron for plants leads to serious diseases, in particular to chlorosis. When photosynthesis and respiration are impaired and weakened as a result of the insufficient formation of organic substances from which the plant's body is built, and the lack of organic reserves, a general metabolic disorder occurs. Therefore, with an acute lack of iron, the death of plants inevitably occurs. In trees and shrubs, the green color of the apical leaves disappears completely, they become almost white, and gradually dry up.

Manganese is absorbed by plants and distributed among their organs as a result of metabolic processes. Passive adsorption takes place, especially at high and toxic levels of its content in the solution. Manganese is distinguished by a high degree of absorption activity and rapid transfer in plants. In plant fluids and extracts, it is present in the form of free cationic forms and is transported in plants in the form of Mn^{2+}, and its significant concentrations are found in young plant organs. One of the most important functions of manganese is participation in redox reactions. Mn^{2+} is a component of two enzymes: phosphotransferase and arginase. In addition, it can replace magnesium in other enzymes and increases the activity of some oxidases. The latter happens, apparently, as a result of a change in the valence of manganese.

Manganese is necessary for normal photosynthesis, participates in the reduction of CO_2, plays a role in maintaining the structure of chloroplasts. In the absence of manganese, chlorophyll quickly breaks down in the light. Manganese activates more than 35 enzymes involved in various reactions, including nitrogen metabolism. Owing to this, it is difficult for plants experiencing a lack of manganese to use nitrates as a source of nitrogen nutrition. In addition, manganese participates in the synthesis of vitamin C, other vitamins and sugars, regulates the water regime, increases resistance to adverse factors, affects fruiting and promotes the acceleration of fruit development.

The lack of manganese greatly affects the intensity of photosynthesis in plants. For example, in oats with a lack of manganese, the intensity of photosynthesis drops by about 2 times. Manganese takes an active part in the release of oxygen during photosynthesis and water splitting. Also, in the absence of manganese, chlorophyll is quickly destroyed in the light. Violation of the photosynthesis system leads to a sharp decrease in the carbohydrate content of the plant, especially in the root part, so the lack of manganese is a key factor in the slowing down of the growth of the root system in plants.

Signs of manganese deficiency in plants most often appear on carbonate soils, on chernozems rich in humus, and on soils with a soil solution pH close to neutral. The highest concentration of manganese is observed in acidic soils, where pH is below 6.5. This feature is explained by the fact that with a decrease in pH by 1.0, the content of mobile manganese in the soil increases by a factor of 10, i.e. liming reduces the content of mobile manganese in the soil, and the use of acidic fertilizers, on the contrary, contributes to its increase. Manganese deficiency is exacerbated at low temperatures and high humidity, so winter and perennial crops are sensitive to its deficiency in spring. The introduction of sulfur, superphosphates (substances that acidify the soil) into the soil increases the content of available manganese. The lack of manganese in the soil is especially acutely felt by cereals, in particular oats, as well as corn, legumes, beets, potatoes, rapeseed, peas, green crops (dill, parsley, spinach, onion, horseradish) apple, cherry, raspberry, grapes [9]. An external sign of manganese deficiency is leaf spot and necrosis.

Zinc has a great influence on oxidation-reduction processes, the rate of which is significantly reduced when it is lacking. Zinc deficiency leads to disruption of hydrocarbon conversion processes. It has been established that with a lack of zinc in the leaves and roots of tomatoes, citrus fruits and other crops, phenolic compounds, phytosterols or lecithins accumulate, and the starch content decreases. The importance of zinc for plant growth is closely related to its participation in nitrogen metabolism. Zinc deficiency leads to a significant accumulation of soluble nitrogen compounds – amines and amino acids, which disrupts protein synthesis. Many studies have confirmed that the protein content of plants decreases with zinc deficiency.

Zinc is part of various enzymes: carbonic anhydrase, triose phosphate dehydrogenase, peroxidase, oxidase, polyphenol oxidase, etc. The importance of zinc for plant growth is closely related to its participation in nitrogen metabolism. Zinc deficiency leads to significant accumulation of soluble nitrogen compounds – amines and amino acids, which disrupts protein synthesis. Many studies have confirmed that the protein content of plants decreases

with a lack of zinc. Under the influence of zinc, the synthesis of sucrose, starch, the total content of carbohydrates and protein substances increase. The use of zinc fertilizers increases the content of ascorbic acid, dry matter and chlorophyll. Zinc fertilizers increase drought, heat and cold resistance of plants [10]. Zn^{2+} ions form complexes with ligands with donor O and N atoms. Zinc is part of the active center of many important enzymes, mainly catalyzing reactions of hydrolysis of peptides, collagen, phospholipids, etc. Zinc activates carbonichydrase enzyme (Fig. 2), which is responsible for the hydration of CO_2 in biofluids and the transfer of H^+ ions to CO_3^{2-}, which regulates one of the most important buffer systems of the body. Zinc-containing enzymes form of «zinc fingers» wonderful shape. This happens because DNA fragments form repetitive domains, which «fold» near zinc ions and characteristic folds – «fingers» appear. The "fingers" include fragments of the type $(Cys)_2(His)_2$, $(Cys)_3(His)$, $(Cys)_4$ or thiolate cluster complexes with bridging cysteine residues.

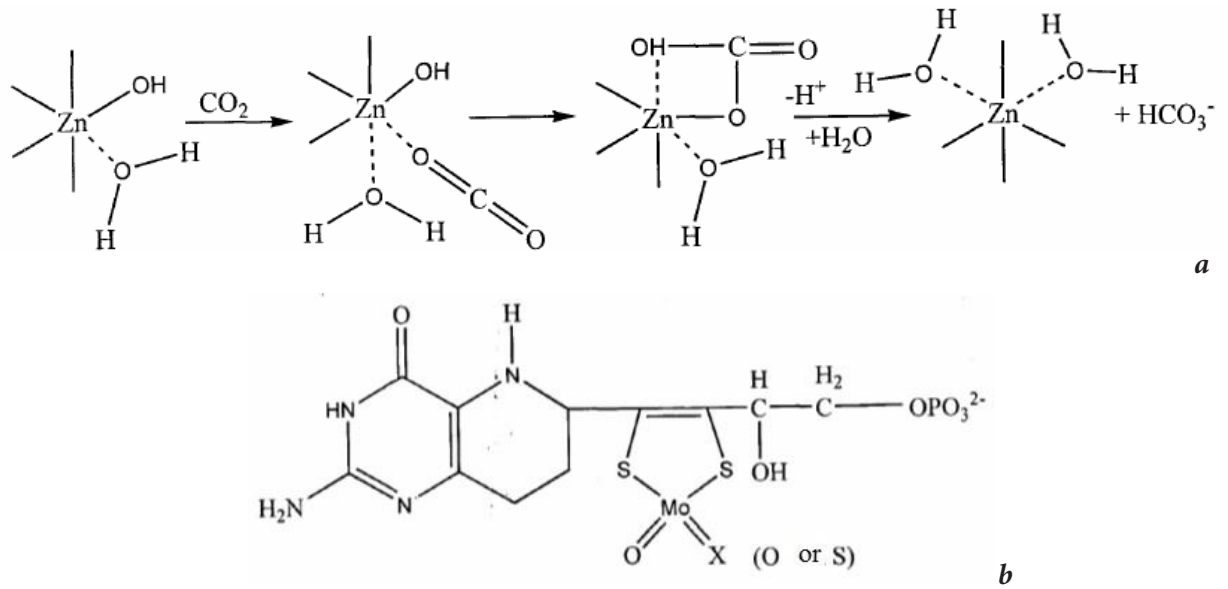


Fig. 2 – Carbonichydrase (a) and a fragment of xanthineoxidase (b).

All cultivated plants in relation to zinc are divided into 3 groups: *very sensitive* (corn, flax, hops, grapes, fruits); *moderately sensitive* (soy, haricot bean, fodder legumes, peas, sugar beets, sunflower, clover, onions, potatoes, cabbage, cucumbers, berries); *slightly sensitive* (oats, wheat, barley, rye, carrots, rice, alfalfa).

Zinc deficiency has the strongest effect on the formation of seeds than on the development of vegetative organs. Symptoms of zinc deficiency are widely found in various fruit crops (apple, cherry, Japanese plum, walnut, pecan, apricot, avocado, lemon, grape). Citrus crops especially suffer from the lack of zinc. With zinc deficiency, chlorotic spots appear on the leaves of plants, which become pale green, and in some plants they are almost white. In apple, pear, and walnut trees, zinc deficiency develops the so-called rosette disease, which is expressed in the formation of small leaves at

the ends of branches, which are arranged in the form of a rosette [11]. With zinc starvation, few fruit buds are laid. The grain yield drops sharply. Among field crops, zinc deficiency most often manifests itself in corn in the form of a white sprout or a white tip. An indicator of zinc starvation in legumes (haricot bean, soybeans) is the presence of chlorosis on leaves, sometimes asymmetric development of the leaf blade. The lack of zinc for plants is most often observed on sandy and sub-sandy soils with a low zinc content, as well as on carbonate and old plowed soils.

In plants, *cobalt* affects the accumulation of nitrogenous substances and carbohydrates, increases the intensity of respiration and photosynthesis, contributing to the formation of chlorophyll and reducing its decay in the dark. Cobalt also increases the overall water content of plants, especially during droughts, and is absolutely necessary for the growth of nodule bacteria and their nitrogen fixation. In plants, this element is found in ionic form and in the composition of vitamin B_{12} (about 4.5%). Plants, like animals, do not synthesize vitamin B_{12}. It is produced by the bacteria of nodules of leguminous plants and participates in the synthesis of methionine. It is part of vitamin B_{12}, which is present in the nodules, and has a noticeable positive effect on the activity of enzyme hydrogenase, and also increases the activity of nitrate reductase in the nodules of legume crops. This trace element affects the accumulation of sugars and fats in plants, has a beneficial effect on the synthesis of chlorophyll in plant leaves, reduces its decay in the dark, increases the intensity of respiration, and the content of ascorbic acid in plants. As a result of foliar fertilization with cobalt in plant leaves, the total content of nucleic acids increases. Cobalt has a noticeable positive effect on the activity of enzyme hydrogenase, and also increases the activity of nitrate reductase in the tubers of leguminous crops. Cobalt takes an active part in oxidation and reduction reactions, stimulates the Krebs cycle and has a positive effect on respiration and energy metabolism, as well as protein biosynthesis of nucleic acids. Due to its positive effect on metabolism, protein synthesis, assimilation of carbohydrates, etc. It is a powerful growth stimulator.

As already mentioned, cobalt is part of cobalamin – coenzyme B_{12} (Fig. 3).

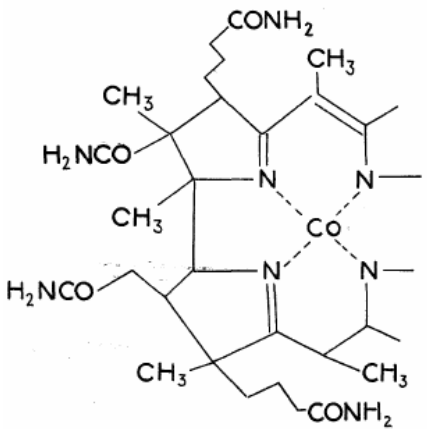


Fig. 3 – Cobalamin fragment near the coordination center.

Cobalamin contains a macrocycle – a corrin ring connected to a nucleotide and dimethylbenzimidazole. The cavity in the center of the corrin ring is occupied by a Co atom with a coordination number of 5, and the sixth coordination position can be occupied by 5-deoxyadenosine, connected to Co through the $–CH_2–$ group. Due to this, coenzyme B_{12} is a rare example of a natural organometallic compound. If the sixth coordination position is occupied by any other small ligands, aquacobalamin, hydroxocobalamin, cyanocobalamin are

formed. In cobalamin, the CO atom can be in 3 oxidation states: +3, +2, +1, and all of them are low-spin. The main enzymatic role of cobalamin is related to the exchange transfer of H or CH_3 radicals between bioligands. Other cobalamin enzymes catalyze radical exchange in the cases of isomerization (mutase) and dehydration (lyase). Radical exchange begins with the weakening of the Co-C bond, which leads to the formation of low-spin 5-coordinated Co(II) and the CH_2R radical, which is replaced by any other radical. CH3 group transfer reactions are based on the high nucleophilicity of the Co^{+1} ion in a square environment. This reaction takes place during the biosynthesis of methionine, as well as for the activity of methanogenic bacteria that produce methane.

Cobalt has a positive effect on the formation of nitrogen-fixing nodule bacteria in legumes, improves the growth and development of plants through the interaction of cell hormones during auxin metabolism, participates in redox reactions, photosynthesis (increases the amount of chlorophyll), synthesis of nucleic acids, promotes the intensity of the passage of respiratory processes, the formation in plants, carbohydrates, fats, sugars, vitamins (ascorbic acid), activates enzymes (in particular nitrate reductase), accelerates the development of vegetative organs, promotes flowering, can accumulate in pollen, forms frost resistance, heat resistance (increases the total water content), increases resistance to stress - factors, diseases, in cereals (resistance to lodging), increases productivity, improves the quality of grown products, promotes better absorption of nitrogen, potassium, phosphorus, magnesium from the soil and limits the entry of heavy metals into the organs of agricultural plants. Cobalt can move freely from the leaves to other organs of the plant, which is an important indicator in foliar feeding [12, 13].

Copper is an essential redox-active transition metal that is involved in many physiological processes in plants because it can exist in multiple oxidation states *in vivo*. Under physiological conditions Cu exists as Cu^{2+} and Cu^{+}. Cu acts as a structural element in regulatory proteins and participates in photosynthetic electron transport, mitochondrial respiration, oxidative stress responses, cell wall metabolism and hormone signaling. Cu ions act as cofactors in many enzymes such as Cu/Zn superoxide dismutase (SOD), cytochrome c oxidase, amino oxidase, laccase, plastocyanin and polyphenol oxidase. At the cellular level, Cu also plays an essential role in signaling of transcription and protein trafficking machinery, oxidative phosphorylation and iron mobilization. Thus, plants require Cu as an essential micronutrient for normal growth and development; when this ion is not available plants develop specific deficiency symptoms, most of which affect young leaves and reproductive organs. The redox properties that make Cu an essential element also contribute to its inherent toxicity. Redox cycling between Cu^{2+} and Cu^{+} can catalyze the production of highly toxic hydroxyl radicals, with subsequent damage to DNA, lipids, proteins and other biomolecules. Thus, at high concentrations, Cu can become extremely toxic causing symptoms such as chlorosis and necrosis, stunting, leaf discoloration and inhibition of root growth. At the cellular level, toxicity may result from 1) binding to sulfhydryl groups in proteins, thereby inhibiting enzyme activity or protein function; 2) induction of a deficiency of other essential ions; 3) impaired cell transport processes; 4) oxidative damage [14, 15].

Plants use Cu as a cofactor for a wide range of proteins involved in several physiological processes, including photosynthesis, mitochondrial respiration, carbohydrate metabolism, formation of phenolics in response to pathogen attack, superoxide scavenging, cell wall remodeling, and ethylene perception. The majority of Cu proteins (~90%) found in nature function as oxidoreductases. The most abundant Cu protein in plants is plastocyanin (which utilizes about 50% of Cu in plastids), a protein essential for photosynthetic electron transport in chloroplasts that transfers electrons from the cytochrome b6f complex to photosystem I (PSI). Cu is part of Complex IV of the mitochondrial respiratory chain, and thus is involved in metabolic pathways that supply energy for cellular processes. Other Cu proteins are Cu/Zn superoxide dismutase (dismutation of superoxide), laccase (cell wall remodeling), amine oxidase (cell wall and plant tissue differentiation, wound healing, and response to pathogens), and polyphenol oxidase (wounding and pathogen response) [16].

In plant organisms, copper is found mainly in the form of copper-containing proteins [17, 18]. There are more than 20 enzymes containing copper in the active center, most of which are oxidases. Their biological role is related to the processes of hydroxylation, oxidative catalysis, and oxygen transfer. The role of copper in enzyme cytochrome oxidase, which controls the reactions of the $O_2 \rightarrow H_2O$, $O_2 \rightarrow H_2O_2$ type, as well as the disproportionation reaction $O_{2^-} \rightarrow O^{2-} + O^o$, which is very important for the body, and takes place with the participation of the enzyme superoxide dismutase, has been studied in the most detail. Oxygen carrier proteins include the protein hemocyanin, which is intracellular, which is generally characteristic of Cu-containing proteins (Fig. 4).

In the hemocyanin oligomer, each monomer unit contains 2 copper atoms located very close together. Deoxyhemocyanin is colorless, but acquires a bright blue color when binding O_2. In deoxyhemocyanin, the Cu(I) atom has a coordination number of 3 and pyramidally coordinates 3 histidine residues. After the addition of an O_2 molecule, 2 bridging bonds are formed, which connect 2 copper atoms. At the same time, O_2 is reduced to O_2^{2-}. The protein residues converge significantly, and the Cu atoms have a coordination number of 5, which is typical only for Cu(II).

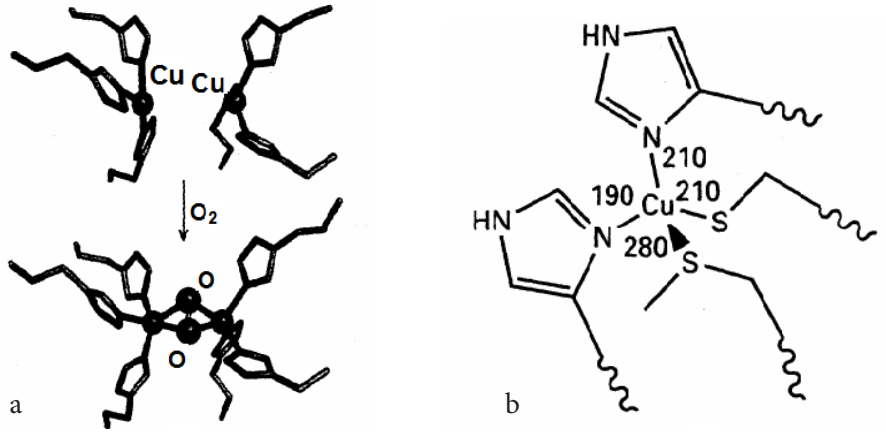


Fig. 4 – Fragment of the structure of copper-containing proteins: hemocyanin (a), plastocyanin (b).

Electron carriers are the so-called "blue" copper proteins containing both Cu(I) and Cu(II), as well as residues of thiolate groups, imidazole, and cysteine. In plastocyanin and azurin, there is a planar Cu(I) complex with a coordination number of 3. When coordinating the fourth ligand, which usually contains a donor sulfur atom, the coordination number of Cu(I) increases to 4 in a tetrahedral environment.

In cytochrome-*C*-oxidase and N_2O-reductase, the center of the enzyme is a binuclear complex in which 2 Cu atoms are connected through a bidentate cysteine residue, and each Cu atom coordinates a heterocyclic imidazole nitrogen atom. In one-electron oxidation of this form, a purple paramagnetic complex is formed, in which the unpaired electrons belong to both copper atoms. Despite the fact that a number of other macro- and microelements greatly affect the rate of redox processes, the effect of copper in these reactions is specific, and it cannot be replaced by any other element. Under the influence of copper, the activity of peroxysylase increases and the activity of synthetic centers decreases and leads to the accumulation of soluble carbohydrates, amino acids and other products of the breakdown of complex organic substances. Copper is a constituent part of a number of the most important oxidizing enzymes – polyphenol oxidase, ascorbin oxidase, lactase, dehydrogenase, etc. All of these enzymes carry out oxidation reactions by transferring electrons from the substrate to molecular oxygen, which is an electron acceptor. In connection with this function, the valence of copper in redox reactions changes from a divalent to a monovalent state and back.

Almost all copper in leaves is concentrated in chloroplasts mainly in the form of plastocyanin and is closely related to the processes of photosynthesis: it stabilizes chlorophyll, protecting it from destruction. Copper is part of copper protein, forming an oxidizing enzyme, and promotes the synthesis of iron-containing enzymes in plants. It positively affects the synthesis of proteins in plants, which ensure the ability of plant tissues to retain water, as a result, copper in the form of fertilizer adds drought and frost resistance to plants and protection against bacterial and fungal diseases. Copper participates in the process of nitrogen fixation by plants, increases resistance to lodging. In practice, copper is used in crop production, especially on poor peat-swamp soils. With its deficiency, young leaves quickly wither and dry without visible signs of chlorosis, abnormal intense shedding is often observed. [19].

When feeding with ammonia nitrogen, the lack of copper delays the incorporation of nitrogen into protein, peptones, and peptides already in the first hours after nitrogen fertilization. This indicates a particularly important role of copper in the application of ammonia nitrogen. A characteristic feature of the action of copper is that this trace element increases the resistance of plants against fungal and bacterial diseases. Copper reduces grain crops diseases of various types of smut, increases the resistance of plants to brown spot, etc. Symptoms of plant diseases with a lack of copper in the soil are manifested for cereals in the whitening and drying of the tips of the leaf blade. With a strong lack of copper, the plants begin to bush intensively, but later earing does not occur, and the entire stem gradually dries up. Fruit crops with a lack of copper suffer from the so-called dry top or exanthema. At the same time, pronounced chlorosis develops between the veins on the leaf blades of plum and apricot trees. In

tomatoes, when there is a lack of copper, the growth of shoots slows down, the development of roots is weak, the appearance of dark bluish-green leaves and their twisting, the absence of flower formation. Copper deficiency negatively affects plant reproduction. Pollen grains are formed in smaller quantities, and for cereals, an empty ear grain is characteristic. [15, 20].

Thus, summarizing the need and behavior of Cu in plants, the following conclusions can be drawn:

1. Cu is mainly complexed with organic compounds of low molecular weight and with proteins.

2. Cu is found in compounds that do not have conducting functions, as well as in enzymes that have vital functions in plant metabolism.

3. Cu plays an important role in several physiological processes – photosynthesis, respiration, carbohydrate distribution, reduction and fixation of N, protein exchange and cell wall metabolism.

4. Cu affects the water permeability of xylem vessels and thus controls water relations.

5. Cu controls the production of DNA and RNA, and its deficiency significantly inhibits plant reproduction (reduction of seed production, pollen sterility).

6. Cu is involved in disease resistance mechanisms. This resistance of plants to fungal diseases is likely to be associated with an adequate supply of Cu. There is also evidence that Cu-enriched plants are susceptible to some diseases. These phenomena may indicate an indirect effect of Cu on plant disease resistance.

Currently, *molybdenum* has been put forward in one of the first places among other microelements in terms of its practical importance, since this element turned out to be a very important factor in solving one of the cardinal problems of modern agriculture – providing plants with nitrogen. With a lack of molybdenum, a large amount of nitrates accumulates in plant tissues and the normal nitrogen metabolism is disturbed [21]. Molybdenum is an essential component in two enzymes that convert nitrate into nitrite (a toxic form of nitrogen) and then into ammonia before it is used to synthesize amino acids within the plant. It also needed by symbiotic nitrogen fixing bacteria in legumes to fix atmospheric nitrogen. Mo is involved in hydrocarbon exchange, in the exchange of phosphorus fertilizers, in the synthesis of vitamins and chlorophyll, and affects the intensity of redox reactions. After seed treatment with molybdenum, the content of chlorophyll, carotene, phosphorus and nitrogen in the leaves increases. It was established that molybdenum is part of the enzyme nitrate reductase, which restores nitrates in plants. The activity of this enzyme depends on the level of supply of plants with molybdenum, as well as on the forms of nitrogen used for their nutrition. With a lack of molybdenum in the nutrient medium, the activity of nitrate reductase is sharply reduced [22, 23].

Molybdenum is able to detect both different oxidation states (+4, +5, +6) and variable coordination numbers (4, 5, 6, 8). Therefore, the biological action of Mo is diverse. It is the presence of Mo that allows leguminous plants to assimilate atmospheric nitrogen, in the body of animals, Mo is part of redox enzymes, including xanthine oxidase, which is involved in the exchange of purines and the transfer of O_2. With an excess of Mo in the soil, it accumulates in the body, which contributes to the activation of xanthine oxidase (Fig. 5) and the synthesis of an excessive amount of uric acid.

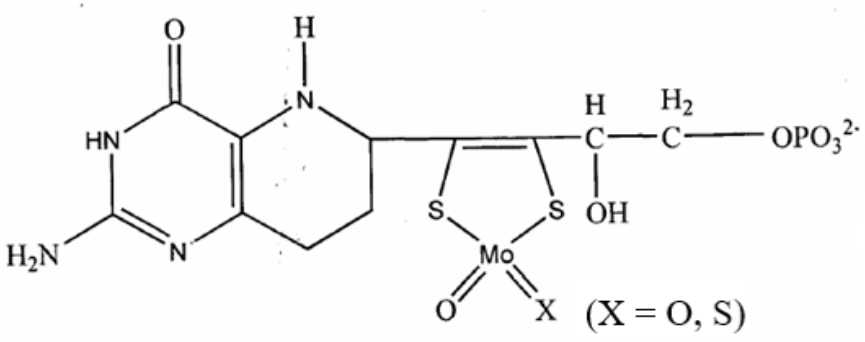


Fig. 5 – Fragment of xanthine oxidase.

Like most metals required for plant growth, molybdenum is used by special plant enzymes to participate in reduction and oxidation reactions. Molybdenum is an integral part of an organic pterin complex called molybdenum cofactor (Moco). The coordination unit of a Mo-containing enzyme is usually formed from thiolate ligands (for example, pterin), cysteine residues and is supplemented with ligands with donor oxygen atoms: water molecules, OH^- and O^{2-} groups. Moco binds to molybdenum-requiring enzymes (molybdoenzymes) found in most biological systems, including plants. When plants are grown under molybdenum deficiency, a number of varied phenotypes develop, which hinder plant growth. Most of these phenotypes are associated with reduced activity of molybdoenzymes. These enzymes include primary nitrogen assimilation enzymes, such as nitrate reductase (NR), and nitrogen-fixing enzyme nitrogenase found in bacteroids of legume nodules. Other molybdoenzymes have also been identified in plants, including xanthine dehydrogenase/oxidase involved in purine catabolism and ureide biosynthesis in legumes, aldehyde oxidase (AO), which is involved in ABA biosynthesis, and sulfite oxidase, which can convert sulfite to sulfate, an important step in the catabolism of sulfur-containing amino acids [22–24].

The value of molybdenum in the life of plants is quite diverse. It activates atmospheric nitrogen binding processes of nodule bacteria, promotes the synthesis and exchange of protein substances in plants. The most sensitive to molybdenum deficiency are such crops as soybeans, grain legumes, clover, and perennial grasses. Plant's need for molybdenum fertilizers usually increases on acidic soils with a pH below 5.2. The physiological role of molybdenum is related to the fixation of atmospheric nitrogen, the reduction of nitrate nitrogen in plants, participation in redox processes, carbohydrate metabolism, and the synthesis of chlorophyll and vitamins. Nitrate reductase with the participation of molybdenum catalyzes the reduction of nitrates and nitrites, and nitrite reductase also with the participation of molybdenum reduces nitrates to ammonia. This explains the positive effect of molybdenum on increasing the protein content of plants. Under the influence of molybdenum, the content of carbohydrates, carotene and ascorbic acid also increases in plants, and the content of protein substances increases. Under the influence of molybdenum, the content of chlorophyll in plants increases, and the intensity of photosynthesis increases.

The availability of molybdenum for plant growth strongly depends on soil pH, concentration of adsorbing oxides (e.g., Fe oxides), degree of drainage of water and organic compounds contained in soil colloids. In alkaline soils, molybdenum becomes more soluble and available to plants mainly in anion form. On the contrary, in acidic soils (pH<5.5), the availability of molybdenum decreases, as the adsorption of anions by soil oxides increases [25]. When plants are grown under the conditions of molybdenum deficiency, a number of different phenotypes develop, which inhibit plant growth. Most of these phenotypes are associated with the reduced activity of molybdoenzymes.

The lack of molybdenum in plants is manifested in the bright green color of the leaves, while the leaves themselves become narrow, their edges curl inward and gradually die, a dot appears, the leaf veins remain light green. The lack of molybdenum manifests itself, first of all, by the appearance of the yellow-green color of leaves, which is a consequence of the weakening of atmospheric nitrogen fixation, the stems and petioles of plants become reddish-brown.

Nickel belongs to conditionally essential elements. Nickel is a component of some plant enzymes, especially urease, which metabolizes urea nitrogen into useable ammonia in the plant. Without nickel, toxic levels of urea can accumulate in tissues; forming necrotic legions on leaf tips. Currently, there is a sufficiently large number of scientific works in which the beneficial effects of Ni compounds on plant growth have been proven [26]. The element Ni is considered an indispensable trace element for plants because it acts as an activator of the urease enzyme. Recent studies have shown that Ni can activate the glyoxalase I isoform, which performs an important step in the degradation of methylglyoxal (MG), a potent cytotoxic compound naturally produced by cellular metabolism. Reduced glutathione (GSH) is consumed and regenerated in the detoxification process of MG produced during stress (stress-induced production). [26, 27] investigated the role of Ni in the interrelation between the MG cycle and GSH homeostasis and suggested that Ni may play a key role in the metabolism of plant antioxidants, especially in stressful situations. Some researchers demonstrated the effect of Ni stimulation on the nitrification and mineralization of nitrogenous compounds [28], and in [29] it was established that microorganisms that metabolize H_2 and urea are highly sensitive to Ni nutrition. It was shown in [30] that water-soluble forms of nickel compounds in small concentrations are easily absorbed by plant roots, which has a positive effect on their development.

In [31] it was found that Ni binds to anionic organic complexes in xylem exudates. Although the transport and storage of Ni appears to be metabolically controlled, this metal is mobile in plants and is likely to accumulate simultaneously in leaves and seeds. It should be noted that Ni is easily and quickly taken up by plants from soils, and until a certain concentration of Ni in plant tissue is reached, adsorption is positively correlates with soil Ni concentrations.

Nickel is found in soil as a free ion and in complexes with other metal ions (such as Fe). In soils, Ni exists in various states of oxidation, but the predominant and more stable form is Ni^{2+}, which exists in a wide range of pH and redox potentials. The biological effects of Ni are very related to its forms, however, regardless of the chemical form of Ni introduced into the

soil, Ni was found in plants only in the form of neutral and negative complexes. Ni cations are included in the structure of many enzymes, including glyoxalases, ureases, methyl-CoM reductases, superoxide dismutases, peptide deformalylases, and some hydrogenases [27, 32, 33]. It plays an important role in ureolysis, methane biogenesis, acetogenesis, hydrogen metabolism, as well as in the maintenance of the cellular redox state, tolerance to stress and protection and optimal use of nitrogen [34–36]. Deficiency of nickel ions in plants causes accumulation of urea and necrotic lesions in plant leaves.

At excessive concentrations of nickel in plants, its phytotoxic effect is manifested – photosynthesis and transpiration are inhibited in plant tissues. At the same time, the development of roots and metabolism lag behind. The most common symptom of Ni toxicity is Fe-induced chlorosis, in which the foliar Fe level is reduced. Another manifestation of nickel toxicity is the reduction of plant growth and photosynthesis caused by induced oxidative stress, inhibition of nitrogen metabolism and enzymatic activity. Thus, nickel salts play a significant role in the growth and development of plants. The absorption of nickel by plants is achieved either by active transport or by passive diffusion, depending on the plant species, soil pH, the form of nickel compounds, their concentration, and the availability of other metals. Solubilized nickel compounds can be transported by various cationic transport systems, such as Fe^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+} in the form of chelates with citric acid, histidine, and nicotiamine, as well as with various proteins, such as permeases, metallothionein, metallochaperones [37–39].

Nickel for plants is an important ultra-microelement that takes part in biological nitrogen fixation. The particular importance of the element lies in the increase of resistance to negative manifestations of the environment, which significantly affects the increase in productivity. Nickel is responsible for the hydrolysis of urea in the plant body (conversion of urea into ammonium (NH^{4+}), as it is an indispensable component of enzyme urease. Nickel has fungicidal properties due to the fact that it directly affects pathogenic organisms or activates the protective properties of the crop. In addition, Ni is the main nutrient for nitrogen-fixing bacteria.

USAGE OF MICRO ELEMENTS IN CROP GROWING. In total, about 75 chemical elements of Mendeleev's periodic system were found in plant cells, which are part of enzymes, hormones, vitamins and other biologically active compounds. Each of the elements performs its specific function and ensures the normal growth and development of crops. Microelements («metals of life») are necessary for the construction of enzyme systems (biocatalysts) for all plants, and it is impossible to replace them with other macro- or meso-elements. For normal life, crops need more than 30 trace elements in sufficient quantities, including both metals (Cu, Zn, Co, Mo, Mn, etc.) and non-metals (I, Si, Se, Br, F, etc.), which are part of various chemical compounds contained in the soil (Table 2.).

When there is a lack of available forms of boron, manganese, copper, molybdenum, and in certain conditions also cobalt, zinc, iodine, vanadium and other microelements in the soil, specific diseases of crops are observed, they give a low and inferior yield. In this case, the use of appropriate microfertilizers eliminates plant diseases and significantly increases the

yield and quality of crop production. Under the action of microelements, the sugar content of many plants increases, the content of starch or protein, vitamins and fats increases. The resistance of plants to drought, high and low temperatures also increases, their susceptibility to pests and diseases decreases. The value of trace elements goes far beyond crop production, as many animal and human diseases are often associated with a lack of trace elements.

Table 2.

Physiological need of agricultural crops for trace elements [40].

Crop/trace element	B	Cu	Fe	Mn	Zn	Mo
Corn	**	**	**	**	***	*
Sorghum	*	**	***	***	***	*
Soy	*	*	***	***	**	***
Wheat	*	***	*	***	*	*
Barley	*	***	*	**	*	*
Pea	*	*	*	***	*	**
Sunflower	***	**	*	**	**	*
Sugar beet	***	**	**	***	**	**
Rape	***	*	*	***	*	***
Flax	**	***	*	*	***	*
Tomatoes	**	**	**	**	**	*
Cucumbers	*	**	*	***	*	*
Onion	***	**	***	**	**	***
White-headed cabbage	***	**	*	***	**	***
Cauliflower	***	**	*	**	*	***
Carrot	***	***	*	***	*	*
Potato	**	*	*	**	**	*
Grape	***	**	***	***	***	*
Apple tree	***	**	***	***	***	*

*** - *key microelement*; ** - *vital microelement*; * - *an important microelement*

A deficiency in the soil of certain trace elements can be detected by the appearance of specific signs in the appearance of plants. However, in the practice of agriculture, one has often to meet with a less acute shortage of trace elements, when clear external signs are not observed, but the growth and development of plants are suppressed and they give low yields. The need for the use of microfertilizers can be de`termined based on the results of a chemical soil analysis for the content of plant-available forms of microelements. With the greatest accuracy, the need to apply microfertilizers in specific soil and climatic conditions can be judged by the results of field experiments. A higher efficiency of using microfertilizers, as a rule, is observed when plants are well supplied with the main nutrients - nitrogen, phosphorus and potassium. At the same time, the introduction of the necessary trace elements

significantly increases the effect of nitrogen, phosphorus and potassium fertilizers. When microelements are introduced, a better use of nutrients from the soil and mineral fertilizers by plants is ensured.

But only a small part of trace elements in the soil solution is in a mobile form, easily absorbed by plants. Therefore, when filling their lack, the form of compounds (degree of availability for the plant organism) in which they will be in the soil should be taken into account. Most trace elements are part of enzymes and act as active catalysts that accelerate important biochemical reactions in plants. Insignificant amounts of microelements in combined action strengthen their catalytic functions and greatly influence the course of life processes in crops. In addition, they affect the orientation of biochemical processes. For example, copper protects chlorophyll from destruction and contributes to an almost twofold increase in the doses of nitrogen and phosphorus. Manganese regulates the ratio of divalent and trivalent iron in plant cells. Boron and manganese have a positive effect on the recovery of crops after freezing, they contribute to the flow of photosynthesis in them. Microelements are of decisive importance in activating the regenerative functions of tissues and resistance of the plant organism to various diseases. They are indispensable in increasing the immunity of plants and reducing their susceptibility to parasitic diseases. Only the complete supply of plants with all the necessary trace elements allows crops to fully use energy, water and basic nutrients (nitrogen, phosphorus, potassium), and as a result, to form higher yields.

Microfertilizers are able to eliminate plant diseases that arose as a result of an incorrect ratio of macroelements (N, P, K) in their nutrition. When one or more microelements are insufficiently supplied to plant cells, there is a decrease in the rate and coherence of the physiological processes responsible for the development of the plant organism. As a result, plants are not able to realize their genetic potential, the level and quality of their yield are significantly reduced. Therefore, along with the main elements of mineral nutrition, which contain macro- and mesoelements, it is necessary to take care of the introduction of complex fertilizers, which contain all the microelements necessary for crops.

The metabolic action and role of each microelement in plants can be characterized in relation to some basic processes, such as:

1. Absorption and transport inside the plant
2. Enzymatic processes
3. Concentrations and forms of occurrence
4. Deficiency and toxicity
5. Ionic competition and interaction

Chemical balance in living organisms is the main condition for their proper growth and development. The interaction of chemical elements also has a similar importance to deficiency and toxicity in plant physiology. Interactions between chemical elements can be both antagonistic and synergistic, and their unbalanced reactions can cause real chemical stress in plants. Antagonism occurs when the combined physiological effect of two or more elements is less than the sum of their independent effects, and synergism occurs when the combined effect of these elements is greater. These interactions can also relate to the ability of one element to inhibit or stimulate the absorption of other elements in plants. All these reactions are quite variable and can occur inside cells, inside membrane surfaces, and also in plant roots.

Below are examples of «interaction»of macro- and microelements in plants [2, 3].

Zinc-phosphorus – a high level of available P causes a deficiency of zinc, which may be associated with the formation of insoluble $Zn_3(PO_4)_2$ in the soil. P-Zn antagonism in roots affects zinc translocation.

Zinc-nitrogen – high levels of nitrogen cause a deficiency of zinc due to increased growth rate with a limiting supply of Zn; retention of Zn in the roots due to the formation of a stable N-Zn protein complex.

Iron-phosphorus – an excessive amount of P and an increase in the P/Fe ratio inactivates iron. This effect is probably due to the formation of a slightly soluble Fe-phosphate precipitate, and the plant is able to absorb and retain Fe in a soluble, mobile form, the amount of which decreases with an increase in the concentration of P in tissues. Similar phenomena occur with copper-phosphorus imbalance in plants.

Molybdenum-sulfur – the absorption of Mo by plants reduces the S content by direct competition between two equivalent anions of the same size; another explanation suggests that the inhibition of Mo utilization in the plant occurs at low Mo levels.

Zinc-magnesium – an increase in the pH of the soil, after the use of $MgCO_3$, causes the interaction of Zn and Mg inside the plant and in the soil.

Zinc-iron – the metabolic functioning of Fe in plants is closely related to the balanced supply of Zn, but with excessive addition of Zn there is a noticeable decrease in the concentration of Fe in plants.

Iron-manganese – Fe and Mn are interconnected in their metabolic functions, the effectiveness of one determines the proportional presence of the other. An excess of Mn reduces the availability of Fe, because Mn prevents the transport of Fe from roots to shoots.

Iron-molybdenum – two effects of Mo and Fe are proposed - a beneficial and a harmful one. With an excess of Mo, there is a deficiency of Fe due to the formation of Fe-molybdate, which leads to a decrease in the content of Fe in the solid body (roots). On the other hand, at an equivalent level of these elements, Mo increases the absorption of Fe.

Copper-iron – in several crops and mainly citrus fruits, Fe-chlorosis occurs due to a high concentration of Cu in the nutrient solution

Copper-molybdenum – the antagonism of Cu and Mo in plants is observed when Cu interferes with the role of Mo in the enzymatic reduction of NO_3.

As mentioned above, plants can easily use trace elements only in a biologically active water-soluble form (mobile form of a microelement), and the immobile form can be used by the plant after complex biochemical processes involving soil humic acids. In the middle of the 20th century, trace elements in crop production were mainly used in the form of inorganic salts of trace elements, which were mainly introduced into the soil in significant quantities. Adding them to the soil contributes to their better assimilation and hence to a more effective effect on the yield of plants. Preparations of this type have a low cost, which attracts the attention of farmers. However, the use of salts of trace elements is appropriate only on acidic and slightly acidic soils. Salts of inorganic acids are poorly soluble, so they are difficult for plants to assimilate. Their excess can cause a toxic reaction and soil salinization. The twenty-first century is the period of the use of more effective preparations of microelements in the

form of chelated microfertilizers. They are more effective due to the availability of trace elements for plants, and act as dual action drugs.

MICROELEMENTS IN CHELATED FORM. Currently, particular attention is given to the role of microelements in living organisms as complexing agents, since most biochemical objects in plants are in the form of coordination compounds [41–43]. Living organisms prefer compounds of those elements that are capable of forming sufficiently strong but at the same time labile bonds. These bonds should be easily subjected to both homolytic and heterolytic rupture as well as cyclization. Such organogens are microelements. The microelements must be introduced into the body in an active form, capable of being transported and absorbed. From this point of view, chelate complexes of biometals are promising [2, 44].

In recent decades, the development of nanotechnology has reached its height. Of particular interest to researchers are nanosystems of a given composition with predicted properties. When used in chemistry, medicine, biotechnology, the size of nano particles or nano-systems is of great importance because it depends on the permeability, activity, solubility and toxicity of nanoparticles [45, 46].

The biocoordination compounds of metals as medical and biological agents form the basis of modern socially and technologically significant innovative developments. Combining metal ions with an organic compound enables the production of supramolecular associates, which are inherently close to the endogenous coordination compounds that exist in the living organism and in general in biosystems. They are less toxic than their constituents and usually have a wide range of biological activity. The attention of the world scientific community to this area is caused by its intensive development, as well as the achievements of biocoordination, bioorganic, medical chemistry. More and more new complexing ions and ligands are involved in the orbit of biochemical research. disorders of plants.

The theory and practice of the experimental chemistry of biologically active substances are related to the development of fundamental principles for the creation of effective drugs based on the structure-activity dependence, which, in turn, is associated with the development of theoretical methods, as well as the accumulation of information on the relationship of molecular structure with biological activity. The effectiveness of the influence of the microelements on any living organism quantitatively and directly depends on the form in which the microelements is.

The twenty-first century is a period of use of more effective chelate-based microelements They are more effective due to the availability of microelements for living organisms and act as dual action drugs. Chelating compounds (chelates) are coordination compounds of metal (microelements) with a chelating agent (chelant, ligand) of a cyclic nature. Complexons are the most promising chelating agents. Complexones belong to complex aminocarboxylic (aminophosphonic) acids, which contain several functional groups: carboxylic (–C (O) O–), phosphonic (PO_3H_2), and amino (NH-) groups. Therefore, thanks to chemical interaction, it is possible to obtain metal-containing compounds in which metal ions will bind to the ligand with the help of electron-donating atoms (oxygen and nitrogen) with the formation of heterocyclic rings (metal-chelate cycles).

Among the multifunctional complex-forming compounds, polyaminocarboxylate, phosphonic, and aminophosphonic complexones are the most promising from a biological point of view for creating microfertilizers [3, 48–50]. In table 3, the most common chelating agents that are currently used to create microfertilizers and in fig. 6 structural formulas of some complexions are shown.

Almost all microelements form fairly stable complexes with the given ligands, while the form of the complexes strongly depends on the pH of the solution or soil. The most favorable conditions for the formation of complexes are non-alkaline environments (pH ~ 5.5–6.5).

In terms of biochemical structure and chemical purity, chelated complexes of microelements are very similar to organometallic compounds synthesized in plant cells (Fig. 7, a, b). Therefore, upon entering a living cell, these substances will be perceived by them not as alien elements, but as «their own», which will ensure their biogenic compatibility and accordingly, high absorption [51–54].

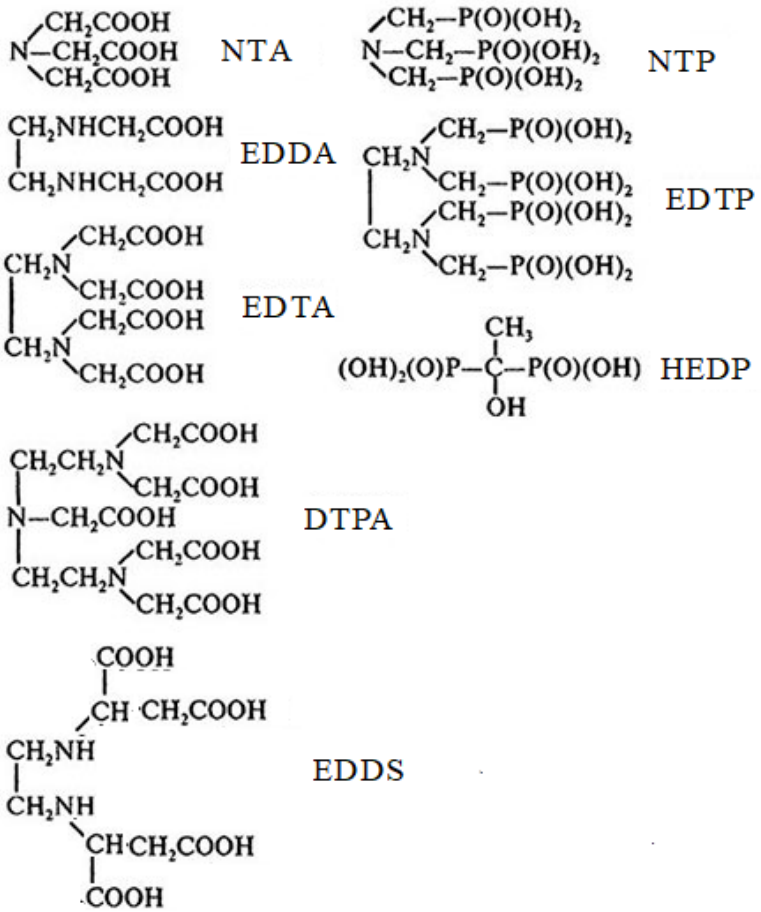
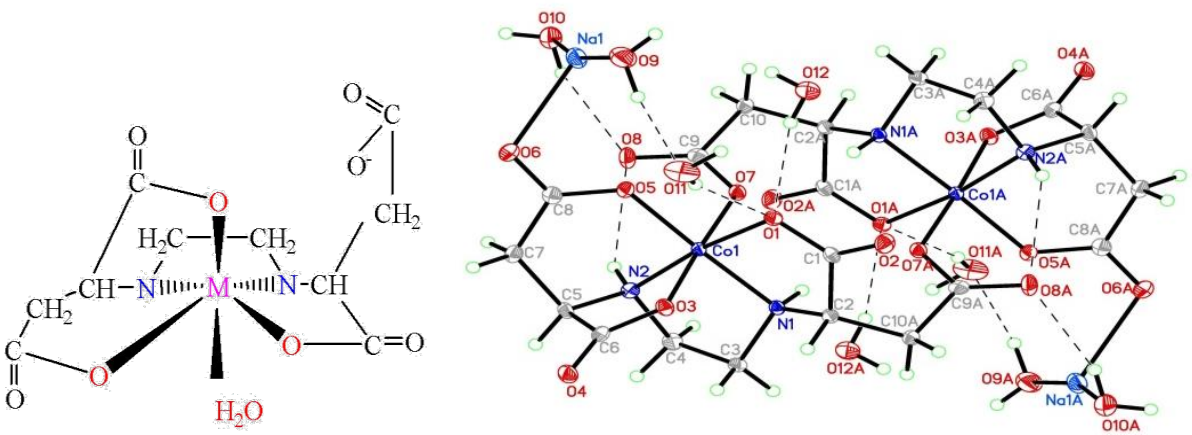


Fig. 6 - Structural formulas of some complexones.

Table 3.

Chelating agents.

Abbreviation	The name of the complexones	Formula
EDTA	Ethylenediaminetetraacetic acid	$C_{10}H_{16}O_8N_2$
DTPA	Diethylenetriaminepentaacetic acid	$C_{14}H_{23}O_{10}N_3$
CDTA	Cyclohexane Tetraacetic acid	$C_{14}H_{22}O_8N_2$
EDDHA	Ethylenediamine-Q-hydroxyphenylacetic acid	$C_{18}H_{20}O_6N_2$
HEDTA	Hydroxyethylenediaminetriacetic acid	$C_{10}H_{18}O_7N_2$
EDDS	Ethylenediaminedisuccinic acid	$C_{10}H_{16}O_8N_2$
NTA	Nitrilotriacetic acid	$C_6H_9O_6N$
EGTA	Ethyleneglyco-bis(2-aminoethylether)tetraacetic acid	$C_{14}H_{24}O_{10}N_2$
HEDP	Hydroxyethylenediphosphonic acid	$C_2H_8O_7P_2$
NTP	Nitrilotrimethylphosphonic acid	$C_3H_{12}NO_9P_3$
EDTP	Ethylenediaminetetraphosphonic acid	
CIT	Citric acid	$C_6H_8O_7$
OX	Oxalic acid	$C_2H_2O_4$



a b

Fig. 7 – General structure (a) and a fragment of molecular structure (b) of transition metal complexes with EDDS [51].

An organic molecule seems to capture metal in a «claw», and when in contact with a plant, the cell membrane recognizes this complex as a substance related to biological structures, and further the metal ion is absorbed by the plant, and the chelant breaks down into simpler substances (Fig. 8) [3, 49, 53].

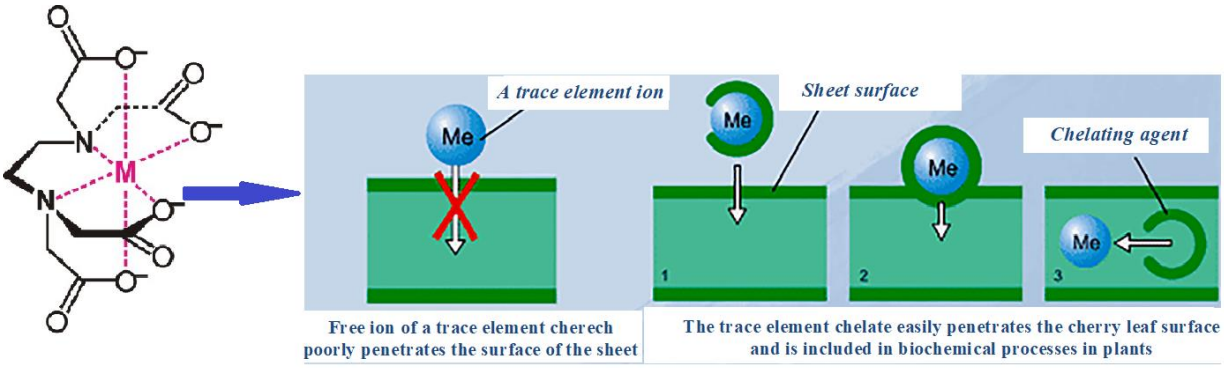


Fig. 8 – The structure of the chelate of a microelement and the action of a chelated microfertilizer on plant leaf rotation.

The complexonates of microelements have a number of valuable properties: they are non-toxic, dissolve well enough in water, have high stability in a wide pH range, and are not destroyed by microorganisms [3, 4, 6]. It is in complexonates that the microelement is transferred into a mobile, biologically active form. The chelate serves to protect the metal ion, prevents it from reacting with the environment and keeps it in a highly soluble form that can be absorbed by plants, even at a pH that naturally leads to their deposition.

The difference between the two forms of microelements (inorganic salts and chelates)is as follows:

• trace elements in the form of inorganic salts work satisfactorily only in acidic soils (pH up to 6). In soils close to neutral, their effectiveness decreases tenfold. In neutral, weakly alkaline and carbonate soils, inorganic salts cannot retain microelements in a water-soluble form available to plants and their efficiency approaches zero, i.e. they change to poorly soluble forms (hydroxides, carbonates) and become unavailable to plants;

• complex ions are stable in all types of soils, and there are no restrictions on soil pH for them;

• microelement complexes are much more effective than ordinary salts, and accordingly their consumption is less. This form of microelements can be used, figuratively speaking, in homeopathic doses, that is, as a prophylactic without even taking into account the composition of the soil and without causing any harm to nature [53].

Among the listed chelants, the most stable complexes are formed by polyaminopolycarboxylic acids (EDDS, EDTA, DTPA, CDTA, EDDHA), which have a high specificity for the iron ion Fe^{3+} at a certain pH. When increasing the pH, the order of stability of the complexes decreases as follows: EDDHA> DTPA> CDTA> EDTA> EDDS (Fig. 9) [3]. It should be noted that EDDHA has a high selectivity for Fe^{3+} in a wide pH range (from 4 to 9), but, unfortunately, this effective chelant forms stable complexes only with iron, and the stability of complexes with other necessary microelements (Mn, Cu, Zn, Co) is significantly lower [55]. Therefore, in the modern practice of creating chelated microfertilizers, the EDDHA complex is used extremely rarely, although it is allowed by the European Union Directive EU 2003/2003 of October 13, 2003 for the production of mineral fertilizers.

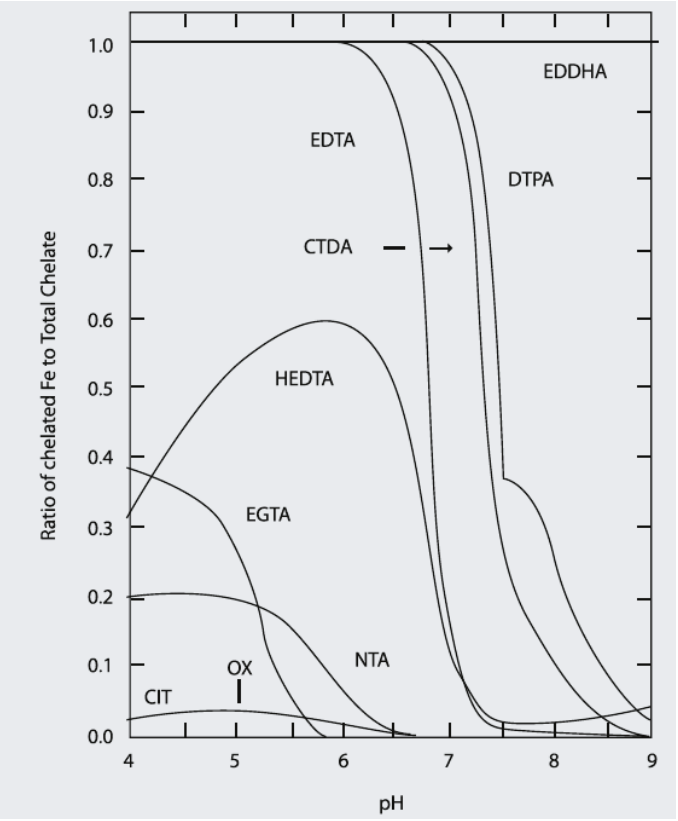


Fig. 8 – Comparison of Fe-chelate stabilities in soil solution [3].

There are various factors affecting the stability of metal chelates, which are primarily related to the nature of metals and the nature of the chelating agent (ligand). The influence of metal ions on the stability of chelates is manifested as follows: at the same degree of oxidation for metal ions of the same family (for example, 3d, alkaline earth elements), the stability of complexes increases with a decrease in the ionic radius. So for Ca(II) complexes lgK_{st}. is higher than for the corresponding strontium complex. For the same metal, as the ion charge increases, the stability constant increases (for example, Fe3+ chelates are more stable than Fe2+ in most cases). And finally, stability depends on the electronegativity of the metal ion and increases as follows: (eV) Cu (1.9) > Fe (1.8) > Zn (1.6) > Mn (1.5) > Ca (1.0), which makes it possible to create a stronger covalent bond.

The effect of stabilization of the complex due to the chelating agent depends on the structure of the ligand (stability increases with the formation of a larger number of metallocycles between the metal ion and the chelating agent), the affinity of cations to the donor atoms of the ligand (for example, for a zinc ion, when coordination bonds with donor atoms are formed, stability changes in the series S> N> O, while for Ca ions there is no signi-

ficant difference between these three donors). The stability of the complexes is significantly affected by the steric effect. When the atoms are too close to each other, energy is wasted due to overlapping electron clouds (Pauli – Born repulsion), and this can affect the desired shape of the molecule (conformation) and reactivity. And different conformations in space have different levels of stability. Complexes that have a high entropy are more stable, since the most stable energy state is achieved in them. For example, for ethylene diamine tetraacetates of various metals, the entropy (ΔS^{25C}) changes in the following order: +55 (Cu^{2+}) = +55 (Zn^{2+})> +42 (Cu^{2+})> +41 (Mn^{2+})> +32 (Mg^{2+}).

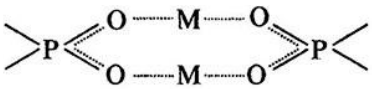
Among complexones that contain carboxyl groups, DTPA is the most optimal, which allows the use of complexones (especially iron) on carbonate soils in a wide pH range (even at pH above 8), where other complexones are ineffective. Although, it should be noted that currently microfertilizers based on EDTA are produced in the largest quantities, which is primarily due to its sufficient availability and relatively low cost.

Currently, the vast majority of chelated microfertilizer preparations are based on complexes of two complexones – ethylenediaminetetraacetic acid and hydroxyethylenediphosphonic acid. The leadership of these chelants is due, first of all, to their unique properties (the possibility of forming complexes with almost all metals of the Periodic System) in combination with a well-developed theoretical and experimental base and, of course, economic feasibility of use. Chelates are produced on the basis of EDTA, which can be used on soils with a pH of less than 8, and for each microelement, stable compounds can be formed only at certain pH values (for example, an iron complex with EDTA is effective in combating chlorosis only on moderately acidic soils; in an alkaline medium it is unstable. It should be noted several characteristic features of complexes with EDTA: complexes with molybdenum are relatively weak, they decompose in an alkaline environment; Ca and Mg chelates are soluble, but less stable compared to other trace elements; no complexes are formed with boron). In addition, chelates with EDTA are decomposed by soil microorganisms, which leads to the transition of trace elements to an insoluble form. These drugs exhibit antiviral activity.

Of the complexones containing phosphonic groups, HEDP is the most promising. On its basis, all individual metal complexonates used in agriculture, as well as compositions of various compositions and ratios, can be obtained. In its structure, it is closest to natural compounds based on polyphosphates (during its decomposition, chemical compounds are formed that are easily absorbed by plants). Chelates based on it can be used on soils with a pH of 4.5–11. A distinctive feature of this chelating agent is that, unlike EDTA, it can form stable complexes with Mo and B. However, it is a very weak chelating agent for iron, copper, and zinc. In the nutrient solution or root zone, these ions are easily replaced by calcium and their effectiveness is significantly reduced. HEDP is resistant to the action of soil microorganisms. The conditions of solubility of HEDP complexes, which are strictly differentiated depending on the complexing metal, make it possible to obtain microfertilizers of prolonged action. The specificity of the interaction of OEDP with calcium ions allows changing the physicochemical and granulometric properties of various mineral fertilizers. It should be noted that the use of HEDP-based chelates in

working solutions on very hard natural waters is unacceptable, however, acidification eliminates this drawback. In addition, HEDP prevents the formation of poorly soluble salts in nozzles, pipelines of nutrient systems and is a growth regulator.

The formation of stable complexes of metals with HEDP can be explained by the formation of chelate structures due to the bidentate coordination of the ligand by two oxygen atoms of phosphonic groups to the cation. At the same time, stable eight-membered cycles are formed, which can be strengthened by intramolecular bonds with the participation of water molecules, formed in the case of the interaction of a metal cation with the oxygen atoms of two phosphate groups at the same time, which can be strengthened by intramolecular bonds with the participation of water molecules:



Hydroxyethylidenediphosphonic acid is close in its structure to natural compounds based on polyphosphates (its decomposition produces chemical compounds easily digested by plants).

Other complexones are also used as chelating agents, for example, ethylenediamine (2-hydroxy-4-methylphenyl)acetic acid. Chelates based on it can be used in pH ranges from 3.5 to 11.0. However, the cost of this highly effective agent is quite significant. The issues of the use of 3-d metal complexes based on ethylenediaminedisuccinic acid are covered quite widely in the literature. These complexes are very stable (lgKst.~13–18) in a wide pH range (3–10) and are biologically active, non-toxic and environmentally friendly compounds [56, 57]. The type of chelating agent strongly affects the efficiency of the fertilizer and the degree of assimilation of trace elements by the plant: chelates based on lignins are absorbed 4 times better, those based on citrates 6 times better, and those based on classical aminopolycarboxylates and/or polyphosphonates (EDTA, HEDP, DTPA) – in 8–10 times better than traditional inorganic fertilizers [58]. In chelated microfertilizers based on traditional complexones such as EDTA, DTPA, NTA, HEDP, the active component is only the ion of a biologically active trace element, and the organic part of the compounds performs only a transport function – diffuse delivery of trace elements to plants. In complexes based on EDDS, the chelant not only delivers the trace element, but also has a biological activity itself. Upon entering to a living organism, the organic part of ethylene diamine disuccinates under the influence of sunlight or UV radiation breaks down into essential amino acids (arginine, leucine, isoleucine, valine, histidine, asparagine, alanine), which are present in the living organism as components of the metabolic chain (Fig. 9, table 4) [59–61].

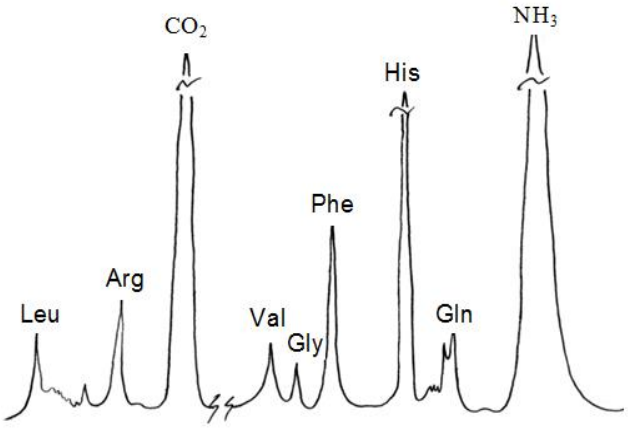


Fig. 9 – Chromatogram of photolysis products of Fe^{III}EDDS model solutions (C=1·10^{-3} mol/l) after irradiation λ=345 nm [60, 61].

Table 4.

Products of the photochemical decomposition of Fe(III) and Mn(II) complexonates with ethylenediaminedisuccinic acid.

FeEDDS	MnEDDS
NH_3 – 68%	NH_3 – 89%
CO_2 – 82%	CO_2 – 68%
–	Alanin (Ala) – 0,35%
Arginine (Arg) – 6,3%	Arginine (Arg) – 3,89%
Asparagine (Asp) – 1,9%	Asparagine (Asp) – 1,8%
Valine (Val) – 0,72%	-
Histidine (His) –13,9%	Histidine (His) – 9,8%
Isoleucine (Ile) – 0,76%	Isoleucine (Ile) – 0,87%
Leucine (Leu) –1,4%	Leucine (Leu) – 2,7%
Glutamine (Gln) – 1,34%	–
Phenylalanine (Phe) - 11,3%	–

Depending on the 3d-metal, a different set of essential amino acids is formed when the complexes decompose, which is obviously associated with the different nature of the metal and the stability of the complexes. But the main decomposition products are ammonia and CO_2.

The given data show that compounds, the cation of which can change the valence state, undergo photochemical decomposition in solution. The photodecomposition of complexes is accompanied, first of all, by decarboxylation processes with release of free CO2, as well as ammonia. The depth of decomposition increases with increasing pH and the intensity of irradiation. Since the final products of the photolysis of complexonates are natural amino acids containing residues characteristic of the EDDS molecule, it can be assumed that the photodecomposition is accompanied not only by the breaking of the bond in the original EDDS molecule, but also by the recombination of the emerging intermediate products.

The question of the important role of photochemical redox reactions of iron-containing chelates (the transition of Fe(III) to Fe(II)) is discussed in [62]. For the implementation of metabolic processes in plants, a divalent form of iron is needed. The key value of Fe(II) is determined, on the one hand, by the better solubility of its mineral salts compared to Fe(III), and, on the other hand, by the lower stability of Fe(II)-chelates, which facilitates the release of iron from transport forms and its further incorporation into metabolism. The photoreduction of Fe(III) to Fe(II) occurs under the action of optical radiation with wavelengths less than 420 nm. Optical radiation with a wavelength distribution in the range of 350–700 nm is able to penetrate the green leaf and cause photoreduction of Fe (III) in the nutrient solution. This process occurs both with direct irradiation of

solutions and with their illumination through leaves affected by chlorosis. With the exclusion of the ultraviolet part from the composition of optical irradiation, the photoreduction of Fe (III) is suppressed. The stimulating effect of UV radiation on the reduction of Fe(III) and the synthesis of chlorophyll in leaves was found in experiments with soybean plants, in which, under the influence of UV rays, physiological effects were enhanced and accompanied by an increase in the amount of chlorophyll and carotenoids.

The mechanism of photolysis of carboxyl-containing chelates of iron and other trace elements (Mn, Co) consists in the elimination of the CO_2 molecule and the consequent reduction of the chelate cycle. During photolysis, intermediate products with metal-carbon bonds are formed. These products are thermally unstable and form metal ions as well as ligand radicals. For example, the photodecomposition of Fe-chelates of citric or tartaric acids is accompanied by the formation of numerous intermediate compounds, and the end products of decomposition are acetone and carbon dioxide. During the photodecomposition of EDTA, the following products have been identified: carbon dioxide, formaldehyde, ethylenediaminetriacetate, ethylenediaminediacetate ions.

In [61], based on the results of mass spectrometry of metal complexes with ethylenediaminediansuccinic acid, it was established that the decomposition of the compounds is accompanied by the breaking of the C–N bond and intramolecular rearrangement along the labile bonds of the ethylene bridge with the formation of certain amino acid radicals or amino acids themselves. (Table 5).

Table 5.

Ratio of the mass to the charge of fragments and their interpretation in the mass spectra of Fe (III) and Mn(II) complexes with EDDS.

m/z			Fragment	Interpretation
EDDS	**FeEDDS**	**MnEDDS**		
55	64	–	-NH_2-CH_2-CH_2-NH_2-	Ethylenediamine / Ethylenediamine radical
69	69	69	-HC-NH-$(CH_2)_2$-NH-	Fragment EDDS
–	75	75	-NH-CH-COOH	Glycine
86	84	84	-NH-CH-(COOH)-CH_2-	α- Alanin
96	98	96	-NH-CH(CO-)CH_2-CO-	Asparagine fragment
101	–	–	-CH_2-CH_2-CH(NH)COOH	Aminobutyric acid
112	112	112	-CH(COO-)CH-COO-	Succinic acid radical
–	121	–	HOOC-CH_2-CH_2-COOH	Succinic acid
–	130	–	-NH-CH(COOH)-CH_2-COOH	β-Asparagine
–	149	–	HOOC-$(CH_2)_2$-CH(COOH)NH_2	Glutamic acid
158	–	–	HOOC-CH_2-CH(COOH)NH-$(CH_2)_2$-	–
296	296	–		EDDS

Compared to the mass spectra of pure EDDS, a larger set of decay products is observed in the complexes, because the attachment of a metal to the complex one weakens the carbon-nitrogen bond due to the coordination of the cation of amino groups and increases the mobility of the asparagine fragment of EDDS. The decomposition products of ethylenediaminesuccinic acid and its complexes are mainly natural compounds, which determines the environmental safety and biological activity of both EDDS itself and its complexes with microelements.

The study of the stimulating effect of the FeEDDS complex compared to the effect of the natural growth stimulator heteroauxin (HA) on the growth processes of corn showed that under the influence of the complex, the length of the leaf and root increases by ~ 45%, while heteroauxin increases these indicators by ~ 38% [61]. In this case, the stimulation by FeEDDS by more significant than that by NA precisely on the leaves, which are the surface part of the plant. Presumably, in this case, the photodestruction of the complexonate under the action of natural light is more pronounced.

Under the influence of the FeEDDS complex, the content and heterogeneity of free amino acids (alanine, asparagine, glutamine, glycine, threonine, serine, tyrosine, etc.) in plants increases (Table 6). In general, the total amount of amino acids under the action of the complexing agent increases sharply, in addition, there is an increase in the heterogeneity of free amino acids.

Also, a distinction of their qualitative composition under the conditions of stimulation from that under the conditions of inhibition is the absence of an increase in the «non-damaging2 osmolyte of the cell, while its significant accumulation is observed under saline conditions. This is due to the fact that this is how the plant reacts to stressful conditions for it, when growth processes are inhibited. In addition, this is explained by the different compartmentalization of the enzymes for the synthesis and breakdown of proline located in mitochondria. Under saline conditions, the proportion of proline in mitochondrial membranes decreases and, therefore, its decomposition cannot occur.

Table 6.

The content of amino acids in the leaves of corn seedlings.

Amino acid	Control	Experiment
Alanine	12,20	15,8
Methionine	3,12	0,97
Valin	4,63	1,45
Leucine	6,04	4,53
Isoleucine	5,26	5,34
Proline	8,78	7,35
Threonine	–	3,27
Serin	–	2,44
γ-Aminobutyric acid	7,39	7,68
Arginine	2,39	3,33
Glutamine	4,06	5,55
Asparagine	30,88	33,77
Glycine	2,49	24,01
Lysine	2,45	2,26
Tyrosine	–	1,74
Phenylalanine	–	5,43
Histidine	–	1,66
Amount, %	0,19	0,39

Based on the results obtained, taking into account the data of [63, 64], an assumption was made about the mechanism of action of FeEDDS complexonate in plants.

The tricarboxylic acid cycle (TCAC) is a key step in the respiration of all cells that use oxygen, the intersection point of many metabolic pathways in the body, an intermediate step between glycolysis and the electron transport chain. In addition to a significant energy role, the cycle also performs a significant plastic function, that is, it is an important source of precursor molecules, from which, in the course of other biochemical transformations, such important compounds for cell life as amino acids, carbohydrates, fatty acids, etc. are synthesized. The tricarboxylic acid cycle includes 8 main stages, including the oxidation of isocitrate to α-ketoglutarate, the oxidation of α-ketoglutarate to succinyl-CoA, the conversion of succinyl-CoA to succinate. It was shown in [63] that the amino acids histidine, proline, arginine, glutamine, and glutamate can be converted into α-ketoglutarate and restore its concentration; isoleucine, valine, methionine, tryptophan - into succinyl-CoA, aspartate, phenylalanine and tyrosine into fumarate; aspartate and aspragine to oxaloacetate. The amino acids alanine, serine, threonine, cysteine and glycine can be converted into pyruvate, which is necessary for the tricarboxylic acid cycle (Fig. 10).

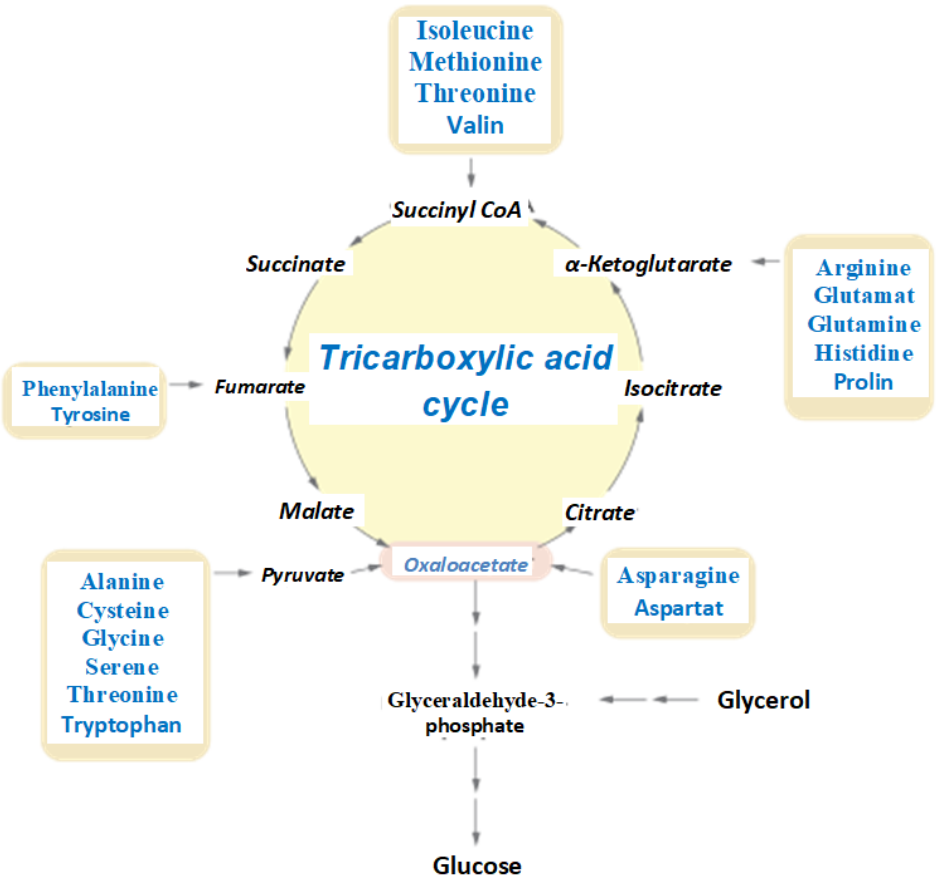


Fig. 10 – Scheme of the inclusion of amino acids in the tricarboxylic acid cycle [63].

In plants, during the glyoxylate cycle, acetyl-CoA is converted into succinate, which is further involved in biosynthetic processes [64].

The increase in the pool of free amino acids in plants under the influence of FeEDDS occurs due to a significant increase in the content of glutamine – one of the main transport forms of nitrogen. As is known that glutamine in the plant is formed from α-ketoglutarate (Fig. 11). The FeEDDS complex includes two succinate fragments. Therefore, it can be assumed that these succinate residues are included in the tricarboxylic acid cycle, going the path to α-ketoglutarate and, thus, accelerate the main substrate- and energy-providing process of the TCAC.

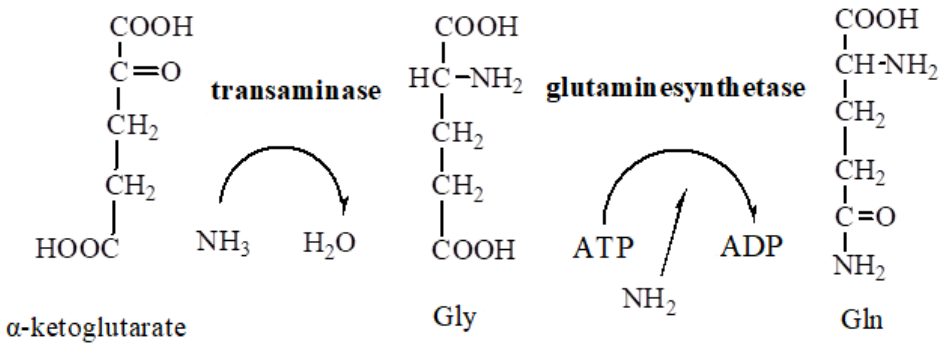


Fig. 11 – Formation of glutamine in a plant cell.

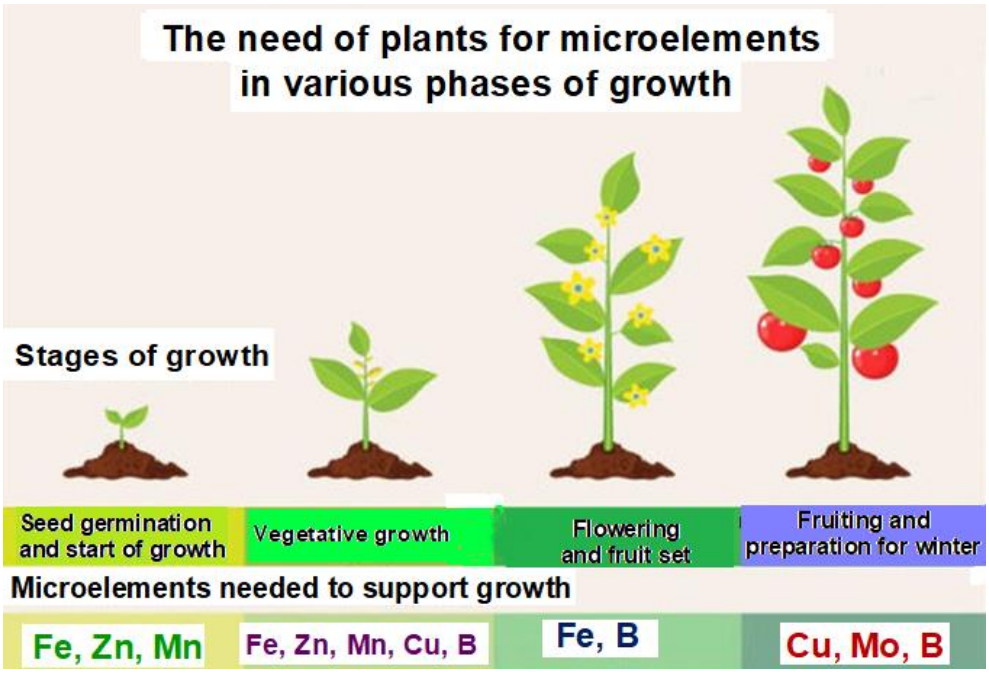


Fig.12 – The need of plants for microelements in various phases of growth.

It is also possible that metal complexes with EDDS somehow activate the path of tryptophan synthesis or are directly included in this path, and tryptophan is a precursor of auxin – a plant growth hormone.

APPLICATION OF COMPLEXONATES OF MICROELEMENTS IN PLANT BREEDING. The use of chelate microelements based on complexonates is very wide, since they allow providing plants with the necessary microelements by converting ME into a mobile biologically active form not only in plants, but also in the soil. Metal complexonates used as microfertilizers are the most effective form of micronutrients and a means of regulating the production process of agricultural crops, both during seed treatment before sowing and during root and foliar top dressing [65]. With their help, you can easily correct nutritional deficiencies that occur as the plant develops (Fig. 12). Especially valuable is the use of chelates at an early stage of development, when the root system is not yet well formed. In the flowering stage, the use of foliar dressings with chelates increases the number of ovaries, and fruit processing increases their sugar content.

Chelates are compatible with insecticides and pesticides and when used together reduce plant stress due to the application of pesticides.

Microelements in chelated form, enhance plant immunity and serve as a prophylactic against fungal and viral diseases.

In complexonates organic acid significantly increases the solubility of the microelement ion in solution; transports the microelement ion into the plant organism; protects the microelement ion from transformations of physical and chemical nature; promotes the rapid involvement of microelement ion in biochemical processes in the plant organism (Fig.13) [3].

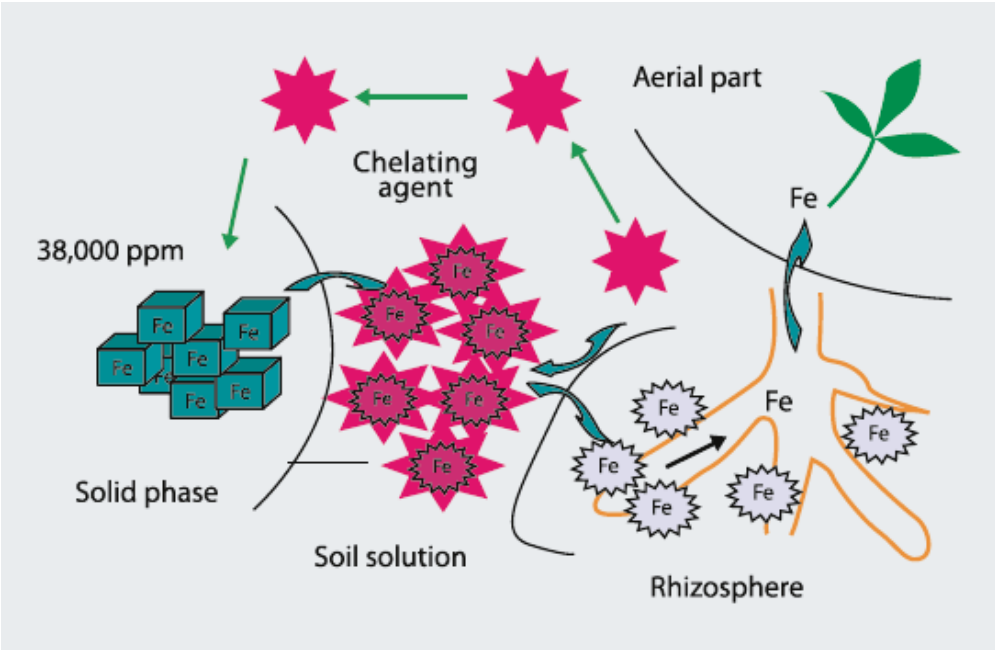


Fig. 13 – Mechanism of metal (Fe) release from chelating agent [3].

The main role of chelates is to keep the metal cations in solution so they can diffuse through the soil to the roots. This is done through the formation of a chelate "ring" around the metal cation, which protects the metal from interaction with other inorganic compounds. Upon reaching the plant root, the metal cation either splits out from the chelate and diffuses into the root membrane, or the entire metal chelate complex is absorbed into the root and then decomposes, releasing the metal. Both cases result in the extraction of the metal up the root, and the chelate is returned to the soil solution for binding other metals.

Applying to the soil and spraying with solutions of complexonates of microelements have a positive effect on the yield of many crops [66–77]. For example, treatment with manganese, iron, copper, etc. Complexonates on based EDTA and DTPA, of the seeds of cereal, industrial, grain crops (buckwheat, oats, barley, rye, flax) lead to a change in the terms of plant vegetation, accelerates the germination of these crops, and increases their yield. In [77] the effect of chelate compounds of zinc, copper, manganese and iron with HEDP on the yield of spring rapeseed, white lupine and oats was studied. For comparison, traditional forms of trace elements were used – vitriol of the corresponding metals. It was found that the chelated forms of microelements had an advantage over their salt counterparts, providing a biomass yield of rapeseed pods higher than the best of the options using sulfate for zinc by 56%, for copper – 38%, for manganese – 42%, as well as an increase in oat grain by 18%. % when using iron. Also, the individual characteristics of plants in relation to the studied microelements were revealed. Thus, the treatment of spring rapeseed with chelates containing zinc and copper contributed to the greater development of generative organs. In [73], a heterometallic complex of magnesium and germanium^{IV} based on HEDP – $[Mg(H_2O)_6]_3[Ge_6(\mu\text{-}OH)_6(\mu\text{-}HEDP)_6]\cdot 20H_2O$ – was used for the pre-sowing treatment of winter wheat seeds. It has been proven that the compound increases the field germination of wheat by 75%. In addition, intensive growth of ground mass (17 cm) and primary root system (7.5 cm) was observed in the plants. These indicators are significantly higher compared to the control and standard – complex fertilizer Novalon.

During clonal micropropagation of the gooseberry cultivar at the stage of rhizogenesis, the efficiency of modification of media with mineral salts according to Quoirin-Lepoivre (QL) was shown by replacing iron, which is standardly used in the form of $FeSO_4\cdot 7H_2O$ together with Na_2EDTA, with chelated forms with carboxyl-containing ligands Fe(III)-EDTA and Fe(III)-DTPA and the organophosphate complexone Fe(II)-HEDP. On the 45th and 60th days of subculturing, the distribution in descending order of the impact of chelate iron compounds on the rooting rate of the studied gooseberry plants was as follows: Fe(III)-EDTA>Fe(III)-DTPA> Fe(II) -HEDP> Fe(III)-EDDHA>Fe(III)-HEDP. On the 60th day of subculturing in the best variants of the experiment, the rooting rate of gooseberry microcuttings of cultivar Pink-2 was 86.7-100% compared to 60% in the control variant [74].

The effect of organic (Fe-EDTA and Fe-EDDHA) and inorganic ($FeCl_3$) iron substances on the rooting of the rootstock GF-677 (*Prunus amygdalus*×*Prunus persica* – hybrid of peach and almond) in vitro was studied. Full rooting (100 %) was observed in explants nourished with Fe-EDDHA, while less

rooting was found in the absence of iron or in the presence of FeCl3. On the contrary, no root formation was observed in explants nourished with Fe-EDTA, which showed extremely lower chlorophyll and high iron contents at the end of the experiment [71].

Complexes of 3d-metals with EDDS are environmentally safe biostimulants and positively affect the yield of plants (apple trees, strawberries, legumes, cabbage, buckwheat, alfalfa, etc.) [72, 74–77]. Fe[S,S']-EDDS was evaluated as an iron-containing fertilizer in growing calendula [78]. It has been shown that FeEDDS complexes are a suitable source of Fe for the production of marigolds and, most likely, other horticultural crops. Iron sources (FeEDDS, FeEDTA, FeDTPA, FeEDDHA, and $FeSO_4$) did not affect marigold leaf count, plant height, dry weight, or leaf greenness, and there was no evidence of bronze spotting or micronutrient toxicity syndrome. At the same time, all the main indicators of the development of calendula leaves when using chelate complexes and ferrous sulfate did not differ much and were sufficient for normal growth. However, obtaining concentrated initial solutions of fertilizers with non-chelate microfertilizers turned out to be practically impossible due to the low solubility of the iron salt. Therefore, APCA complexones (chelates) are necessary to maintain the solubility of this metal. And the best fertilizer to use are FeEDDS/EDDS chelates.

In [79], it was established that no negative consequences are observed when using FeEDDS on peat soils to increase the yield of fruit and vegetable crops. The work [80] compared the mobility, leaching and availability of ionc of zinc when using its various complexonates (ZnHEDTA, ZnEDDHSA, ZnEDTA, Zn(S,S)EDDS) on haricot bean. It was established that the maximum concentration of zinc in soil leachate was 65 mg/l for Zn(S,S)EDDS when 10 mg of Zn was applied per 1 kg of soil. At the same time, the pH of the calcareous soil increased significantly over the course of the experiment.

The effect of presowing treatment of spinach seeds with compounds containing complexones (EDDS, IDS), as well as their complexonates with magnesium and zinc, on the content of chlorophylls and carotenoids in plant leaves was studied. The effect of complexons was studied in combination with the exposure of seeds to a weak constant magnetic field. An increase in the content of pigments, participants in the process of photosynthesis, was recorded in spinach plants [81]. In the presence of 50 μmol/L Cu, the addition of edds increased the growth of shoots and roots and decreased the relative loss of electrolyte from the root cells of chrysanthemum (*Chrysanthemum coronarium L.*), which led to an increase in the accumulation of copper in plant shoots [82].

The results of studies of the effect of EDDS and its complexes with boron showed a significant efficiency of using borate complexes in comparison with the traditional boron microfertilizer H_3BO_3 as stimulators of soil biological activity and photosynthetic processes in order to obtain an optimal yield of table beet root crops [83]. It has been proven that EDDI-AC has a pronounced antimicrobial effect, and B-EDDS stimulates the microflora. Treatment with B-EDDS solution caused an increase in leaf weight by 19% and in root crops by 37%. The effect of boron compounds on the germination, biomass, and pigment composition of seedlings of flax, wheat, and Kalanchoe pinnate, as well as on the nutrient content of Jerusalem artichoke tubers, was studied [84]. Seed

germination in a solution of boroethylenediamine disuccinate significantly increased the level of chlorophyll content of flax seedlings. Treatment with boric acid and free ligand EDDS also caused some increase in biologically active substances. Apparently, not only boron, but also EDDS is included in the metabolic processes of the plant as an additional source of organic carbon and amine nitrogen. The obtained data showed that the EDDS borate complex turned out to be a more effective fertilizer for the plant than boric acid or EDDS alone. The use of B-EDDS significantly increased the level of chlorophyll in the leaves and seedlings of wheat, of sugars and pectin in the leaves of Kalanchoe, inulin and fructose in Jerusalem artichoke tubers. Some addition of biologically active substances was also caused by treatment with boric acid and a free ligand. Apparently, not only boron, but also complexone is included in the metabolic processes of the plant as an additional source of organic carbon. At the same time, as part of the complex, both components of the test preparation are more accessible to plants than each separately.

Employees of the V.I. Vernadsky Institute of General and Inorganic Chemistry of National Academy of Sciences of Ukraine have worked, for a number of years to create new chelate forms of microfertilizers based on complexes of Mn(II), Fe(III), Co(II), Cu(II), Zn(II) with EDDS [61, 72, 75, 76 , 85–88]. The effect of complexonates on increasing the yield of fodder (rapeseed, clover, sweet clover, lupine, etc.), technical (alfalfa, buckwheat, corn), vegetable (beets, tomatoes, cabbage) crops, grapes, flowers was studied in a field experiment in different regions of Ukraine. Plants were treated during the period of budding by foliar feeding or pre-sowing treatment of grains with aqueous solutions of preparations with a metal concentration of 0.05 wt.%. It has been established that under the action of complexonates, the yield of plants increases (15–50%), the quality of the fodder mass and grain improves (the content of sugar, fiber, fats and proteins increases). In grape berries, sugar content increases by 10-12%, and in leaves – the content of chlorophylls and carotenoids increases by 59% and 30%, respectively). The use of preparations on flowers significantly increases the number of productive stems: by 22% for carnations and by 42% for roses. In addition, for roses, an improvement in the elitism of the variety was noted – an increase and compaction of buds. In addition to growth-stimulating copper complexes, they exhibit a pronounced fungicidal effect.

The addition of a second biologically active ligand (citric, tartaric acids, thiourea) or metal to ethylenediamine disuccinates made it possible to increase the biological activity of the complexes. For example, when grapes were treated with the heterometallic complex, FeCuEDDS, increased by 7% compared to FeEDDS with monometallic iron complexonate. In that case, the absolute content of chlorophylls and carotenoids increased by 79% and 37% for the monometal complex and by 93% and 48% for the heterometallic complex [87].

On the crops of oats and various herbs (natural meadow grasses), the heterometallic complex CuCoEDDS was tested, which increased the yield of plants by 23% and 13% respectively. Also, in plants, the amount of microelements increases greatly: Cu^{2+} and Co^{2+} (by 38%), crude fat, protein and cellulose (~ 80%) [61]. When lupine and rapeseed plants are treated with solutions of the MnZnEDDS complex, the yield of both crops increases by

20% compared to MnEDDS and ZnEDDS. The content of protein, crude fat and gluten, sugars increases in plant grains (Table 7). At the same time, the efficiency of microelements contained in complexonates is much higher (especially in the case of MnZnEDDS) than when using aqueous solutions of inorganic salts [88, 89].

Mixed-ligand ethylenediaminedisuccinate complexes of iron and copper with hydroxy acids and thiourea (THIO) also increase the yield and quality of grapes, barley, tomatoes, and peas compared to their monoligand counterparts. At the same time, under the action of CuEDDSTHIO, the number of pea plants affected by root rot decreased by 6.2% [61].

Table 7.

Influence of foliar application of the complexes MnEDDS, ZnEDDS, MnEDDS on the accumulation of some metabolites in rape straw and grain.

Option	Crude protein, g/kg		Crude fat, g/kg		Raw gluten, g/kg		Sugar, g/kg	
	straw	grain	straw	grain	straw	grain	straw	grain
control	18,4	169	6,3	353	25,4	109	16,3	35,4
$MnSO_4$	17,7	179	6,2	374	24,7	95	15,5	37,6
$ZnSO_4$	20,4	182	6,6	330	23,8	121	17,2	33,7
MnEDDS	20,0	178	6,6	376	25,7	122	16,9	37,7
ZnEDDS	21,7	175	6,8	342	27,9	128	17,2	38,8
MnZnEDDS	22,6	190	6,8	390	28,6	129	18,0	40,2

It is promising to use 3d-metal complexonates for the treatment of carbonate chlorosis in grapes and fruit and berry crops. The calcareous chlorosis of plants thrives on carbonate soils, which contain from 10 to 50% and more carbonates [80]. In such soils at low pH, the plants are lacking iron and cannot form chlorophyll. However, any soil always contains enough iron. The reason lies in the alkaline reaction of the soil, because there is too much lime, due to which iron is in an insoluble and hence, in an inaccessible form. Due to the lack of access to the plant organism, as well as the partial immobilization of iron already present in its tissues, a situation of deficiency of iron is created. In addition, chlorosis can be caused by the presence of high concentrations of metals such as Mn, Cu, Zn, Co, Ni or Cd, which can compete with Fe on the level of absorption by plants. The external manifestation of the physiological changes caused by iron deficiency is chlorosis of leaves - a change in the color of leaves due to a decrease in the content of chlorophyll in them. When photosynthesis and respiration are impaired and weakened as a result of the insufficient formation of organic substances from which the plant's body is built, and the lack of organic reserves, a general metabolic disorder occurs. Therefore, with an acute lack of iron, the death of plants inevitably occurs. To protect against chlorosis caused by iron deficiency on carbonate soils, preparations containing iron in the form of complexonates are used [80–82]. The accepted mechanism for the treatment of iron chlorosis with iron chelates involves the enzymatic reduction of Fe^{3+}

to Fe^{2+} by the chelate of Fe(III) reductase. The result of this transformation is the release of Fe^{2+}, which is absorbed by the roots, forming a free ligand molecule during the process.

The effectiveness of iron chelate in solving the problem of chlorosis depends on several factors. The first is the ability of the organic compound to efficiently chelate Fe3+ and other metals present in soils (Ca^{2+}, Mg^{2+} and Cu^{2+}). Copper is normally present in soils in low concentrations, but becomes a major competitor to Fe^{3+} due to its ability to be chelated by amino acids. The second factor is the ability of plant roots to remove Fe^{3+} from the chelating agent. This ability is affected by the stability of Fe^{3+} and Fe^{2+} chelates. To predict the reactivity of iron chelates in plants and their effectiveness as chlorosis correctors, it is necessary to know the nature of the complexone and the stability of their complexes with iron, as well as to take into account their photochemical activity. In a series of polyaminocarboxylic complexes, stability increases in the order: FeNTA→ FeEDDHA→ FeEDDS→ FeEDTA→ FeDTPA. Therefore, the antichlorosis effect of more stable complexes is more effective than that of medium-resistant chelates, and even more so of phosphonic complexes, which do not affect the synthesis of chlorophyll in iron-deficient leaves. Obviously, when phosphonic Fe-chelates are applied to the leaf surface, their photochemical inertness prevents the formation of biologically active Fe(II) forms. In turn, the differences in the physiological action between the photochemically active groups of moderately and highly stable Fe-chelates may be due to the unequal period of their photodecomposition. The best antichlorosis effect is possessed by iron complexes capable of intensive but prolonged photochemical destruction [49, 62, 67, 87].

The use of iron(III) complexes in vineyards showed that spraying grape plants affected by carbonate chlorosis and/or affected by freezing has a positive effect on the content of photosynthetic pigments in the leaves and increases the yield of plant berries [49, 61, 87, 90, 91]. Fertilization of chlorotic grape plants with FeEDTA and FeDTPA compounds not only increases the concentration of chlorophyll in leaves, but also reduces the content of organic acids compared to control plants.

USE OF CHELATE COMPOUNDS OF MICRO ELEMENTS FOR PURIFICATION OF PLANTS AND SOIL FROM RADIONUCLIDES. Among the complex systems of measures aimed at minimizing the entry of radionuclides from contaminated soil into the first link of the food chain – the plant, at present and probably in the coming decades, the most effective and economically justified system should be considered the use of mineral and organic fertilizers. When used purposefully in certain forms, quantities, ratios and combinations, they can be used to reduce the input of radioactive substances to agricultural plants by many fold. After the accident at the Chornobyl nuclear power plant, the area most contaminated by radionuclides is the Ukrainian Polissia zone, which belongs to a biogeochemical province, where soils, plants and, accordingly, fodder and products of plant and animal husbandry lack many biogenically important trace elements – iodine, zinc, manganese, cobalt, copper, fluorine, lithium, boron and some others. This is the reason of the wide distribution of specific plant, animal and human diseases in this zone, which are known under the general name of hypomicroelement diseases (various forms of chlorosis, rosette leaves, small leafiness in plants; hypocobaltosis, hypocuperosis,

keratosis, alimentary anemia in animals and humans) [92, 93]. Liming of acidic soils slows down the mobility and inhibits the transition from soil to plants not only of radionuclides, but also of other elements of mineral nutrition. But this is especially reflected in the content of trace elements. In [94] it was shown that under the influence of three times repeated liming of sod-podzolic soil at a dose of 2 t/ha with an interval of 4 years, the content of most of the listed microelements in oat and lupine plants decreased by almost half. It is known that some trace elements, including Zn, Mn, Co, Cu, have radioprotective properties, and some of them can affect the entry of radionuclides into plants and animals. Taking into account the situation with microelements in the region of Ukraine most contaminated with radionuclides, as well as their possible role in anti-radiation protection of living organisms, it is possible to predict their special role in the area affected by the accident. The radiosensitivity of most types of plants is quite high, so the damage from the accumulation of radionuclides by plants and their subsequent transport through food chains to animals and humans is a much more important problem than radiation damage to plants themselves. Therefore, the protective role of the factors that block the entry of radionuclides into plants becomes a more important element of anti-radiation protection than the role of radioprotectors. It is indisputable that the basis of such blocking should be interactions occurring between microelements and radionuclides.

Various interactions are possible between trace elements and radionuclides:

• additive, in which the effect of the components is equal to the total sum of the effects of each component;

• synergistic, when one of the components enhances the action of the other, as a result of which the physiological effect of their mixture exceeds the sum of the effects;

• antagonistic, in which the effect of the action is smaller than the action of each of the components separately and than the total action [95, 96].

Additivity indicates the absence of interaction between elements. Antagonistic effect occurs in cases when one of the elements reduces the concentration of another or competes with it for the places of absorption and further transport, but is unable to replace it in physiological processes. A synergistic effect is observed when one of the elements can partially replace the other in some functions (there can be no question of a complete replacement). Synergistic interaction can occur only in cases where an element is multifunctional and can perform some functions together with other elements. On this basis, depending on the conditions, which primarily include such indicators as the degree of radionuclide pollution, the composition of radionuclides, the granulometric composition of the soil, its agrochemical properties and some other indicators, three main strategies can be applied to reduce the degree of radionuclide entry into plants:

1. Creation of a competitive situation for the arrival of radionuclides on the basis of antagonistic interactions between them and elements of mineral nutrition;

2. Enhancement of the nutrient supply of radionuclide antagonists to plants, based on the synergism between individual elements and

3. Binding (complex formation) of radionuclides in the soil using elements of mineral nutrition (Table 8).

Table 8.

Possible interactions between macro- and microelements and Cesium-137 and Strontium-90.

Antagonism	Element	Synergism
B, Cu, F	N	B, Cu, Fe, Mo
Al, As, B, Be, Ca, Cd, Cr, F, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Si, Sr	P	B, Co, Cu, Mn, Mo, Zn
Al, F, Cd, Cs, Hg, Mo, Rb, Se	K	B, Cu, Li, Mn, Zn
Al, B, Ba, Cd, Co, Cs, Fe, Ns, Pb, Si, Sr	Ca	Cu, Li, Mn, Zn
Al, B, Ba, Co, Cu, Cr, F, Fe, Mn, Ni, Zn	Mg	Al, Zn
As, Ba, Fe, Mo, Pb, Se	S	F, Fe
Ba, Ca, Cd, F, Fe, Mg, Li, Zn	Sr	Pb
Cu, K, Li, Na	Cs	Cd, Ni

It can be seen from table 8 that microelements such as fluorine, iron, cadmium, lithium and zinc, and the macroelements – calcium, barium, magnesium can act as antagonists in relation to ^{90}Sr. Lead is a synergist. In relation to ^{137}Cs, microelements - copper and lithium, and macroelements – potassium and sodium act as antagonists. Synergists of radiocesium are cadmium and nickel. The given tabular data show the second possible relationship between microelements and radionuclides, when microelements contribute to the supply of macroelements to plants, and the latter, acting as antagonists of radionuclides, affect the reduction of their supply to plants.

The creation of a competitive situation between trace elements and radionuclides is based on the interaction of ions of elements with chemical properties close enough to compete for absorption, transport and metabolism. At the same time, competition will be more significant for elements and radionuclides with similar sizes of ionic radii, charge, geometry of coordination and electronic configuration. The selection of antagonists can be carried out not only within one group of the periodic system, but also among the elements of other, as a rule, neighboring groups, among elements of variable valences.

Research on the influence of trace elements on the uptake of radionuclides (137Cs, 90Sr) into plants was conducted mainly on contaminated soils in the northwestern part of Ukraine. A group of researchers under the leadership of Academician I.M. Gudkov. made a series of field experiments in the zone of Ukrainian Polissia to test the most promising trace elements: zinc, manganese, cobalt, copper, molybdenum, lithium, boron and nickel [94, 97–100]. When selecting them, a complex of indicators was taken into account: physiological role, deficiency in the environment, possible antagonistic interactions with radionuclides, possible synergistic interactions with macroelements-antagonists of radionuclides, as well as radioprotective properties. The results of these studies indicate that, under the influence of trace elements, the accumulation coefficients ($K_{accum.}$ – the ratio of the radionuclide content of plants to the content in the soil) of both radionuclides significantly

decreased both in comparison with the control without fertilizers and against the background of the main fertilizer (nitrogen-phosphate). The most effective trace element was zinc, under the influence of which the KN in oat and lupine grains in the version without fertilizers decreased by 2–2.5 times. Manganese and cobalt were somewhat less effective, copper, lithium and boron were even less effective. It should be noted that the effectiveness of microelements was the greatest in the variants without fertilizers and the least against the background of increased doses of fertilizers. This is quite natural, since, firstly, with fertilizers, a certain amount of the most diverse microelements is always introduced into the soil in the form of impurities. And, secondly, in favorable conditions for the growth and development of plants, which are provided by fertilizers, the action of all factors, both positive and negative, is affected to a lesser extent. When foliar feeding of plants (lupine, rapeseed, etc.) with aqueous solutions of zinc, manganese, cobalt, and copper sulfates in plants, the accumulation of 90Sr in the vegetative mass (straw) and seeds decreases by 25–40%, and 137Cs that of by 1.5 times [89 , 101–103].

Complexionates of microelements are much more effective in reducing the accumulation of radionuclides in plant products compared to their inorganic salts. Numerous works have shown that the treatment of various plants with complexonate solutions helps to reduce the specific radioactivity of both ^{137}Cs and ^{90}Sr by several times. For example, the work [104] presents the results of a three-year study the foliar fertilization of spring wheat crops of the Struna Myronivska variety with aqueous solutions of zinc, manganese and their chelated analogues with EDTA in different phases of plant growth and development for the accumulation of some trace elements in grain and straw. It was established that in the early phases of plant growth and development (spraying in the tillering phase), there is an increase in the concentration of both zinc and manganese at the time of harvesting in both grain and straw, but for the most part such growth does not increase the yield of either grain or straw. In the case of foliar fertilization of wheat crops, especially with a zinc solution, the accumulation of iron, potassium, manganese, copper, zinc, and especially boron ions by plants from the soil increases by 1.5–2 times both in grain and in straw compared to the plants of the control variant. When feeding plants with a MnEDTA solution, a similar increase in the coefficients of accumulation of the specified microelements is observed. At the same time, the transition of ^{137}Cs from the soil to grain decreases by 30–35%. The highest effect of reducing the levels of contamination of wheat grain with radiocesium is observed when feeding plants with a solution of zinc complexonate in the first half of the growing season – in the phases of tillering and stooling.

In [105] presents long-term studies on determining the accumulation coefficients of ^{137}Cs and ^{90}Sr in the soil and grass of alpine pastures in Switzerland. The long-term behavior of radionuclides was quantified using the effective half-life, which combines all processes that cause a decrease in activity in a given environment, such as leaching, fixation, erosion and radioactive decay. The results showed that ^{90}Sr is more transferred from alpine soil to grass than ^{137}Cs. This is explained by stronger fixation of Cs in soils. At the same time, the lower the concentration of calcium in the soil, the higher the absorption of ^{90}Sr by grass. This is a very important fact, since it is traditionally believed

that radio-Sr, accumulating together with calcium in the skeleton, poses a threat only to blood cells. But it is well known that calcium is the main mineral component of plant cell membranes and accumulates in increased amounts in the nuclear envelopes of all types of cells. Therefore, the high absorption of ^{90}Sr by plants contributes to the purification of soils from radionuclide pollution, which is an integral part of phytoremediation. A similar conclusion can be drawn regarding radio-cesium.

Thus, some microelements can block the transfer of radionuclides both from the soil to plants and from plants (forage) to the body of animals, thus reducing their accumulation in crop and livestock products. Microelements can influence certain aspects of metabolism in both plants and animals, the activity of metal-containing enzymes, permeability of membranes.

An intensive study of the effect of chelated microelements on reducing the accumulation of long-lived radionuclides ^{137}Cs and ^{90}Sr is being conducted at the Zhytomyr National Agroecological University (from 2020, Polis National University) under the leadership of Ph.D of Agricultural Sciences V.M. Bidenko [106–112]. Chelated microfertilizers based on mono- and heterometallic complexonates with EDDS for field experiments were provided by a group of scientists of the Institute of General and Inorganic Chemistry named after V.I. Vernadsky National Academy of Sciences of Ukraine. The effectiveness of microelement complexonates (Zn, Co, Mn, Cu) was determined under the conditions of field experiments on sod-podzolic soils of the Zhytomyr region on various agricultural plants (wheat, rye, oats, corn, lupine, rapeseed, clover, etc.). The results of experiments show that foliar feeding of lupine, vetch, clover, etc. plants with microelement complexonates helps to reduce the content of Cs-137 and Sr-90 in the green mass of the studied crops. For example, the 137Cs activity of lupine green mass in the control was 671 Bq/kg, in the variants of using Mn and Zn sulfates, the ^{137}Cs content was equal to ~ 440 Bq/kg, and in the areas where mono- and heterometallic complexes (ZnEDDS, MnEDDS, MnZnEDDS) were used, the ^{137}Cs content was only ~350 and 260 Bq/kg, respectively. That is, microelement complexonates contributed to a decrease in the specific activity of Cs-137 by more than 50% (Fig. 14, a). Both microelements showed a high radio-blocking effect. Thus, zinc in the form of a salt solution reduced the accumulation of radio-cesium by more than 1.5 times), and in the form of ZnEDDS – by 2.1 times. The results of the action of trace elements on the accumulation of ^{90}Sr in plants were distinguished, first of all, by high coefficients of accumulation of the radionuclide ($K_{acum.}$=4.33). The influence of microelements in the form of salts on the accumulation of ^{90}Sr in lupine plants was manifested to a somewhat lesser extent compared to monometallic complexonates. The most effective data, as in the experiments with ^{137}Cs, turned out to be in the version with the heterometallic complex MnZnEDDS – the accumulation of radio-strontium in the vegetative mass of lupine decreased by 34% (Fig. 14, b).

It should be noted that microelements used as microfertilizers contributed to the activation of metabolic processes in plants through phytohormones, enzymes, vitamins, improvement of metabolic processes in chlorophylls, contributing to the accumulation of metabolites in crops. In addition, under the influence of complexonates, an increase in some microelements was observed in plants compared to the control: copper, zinc, iron and manganese [113].

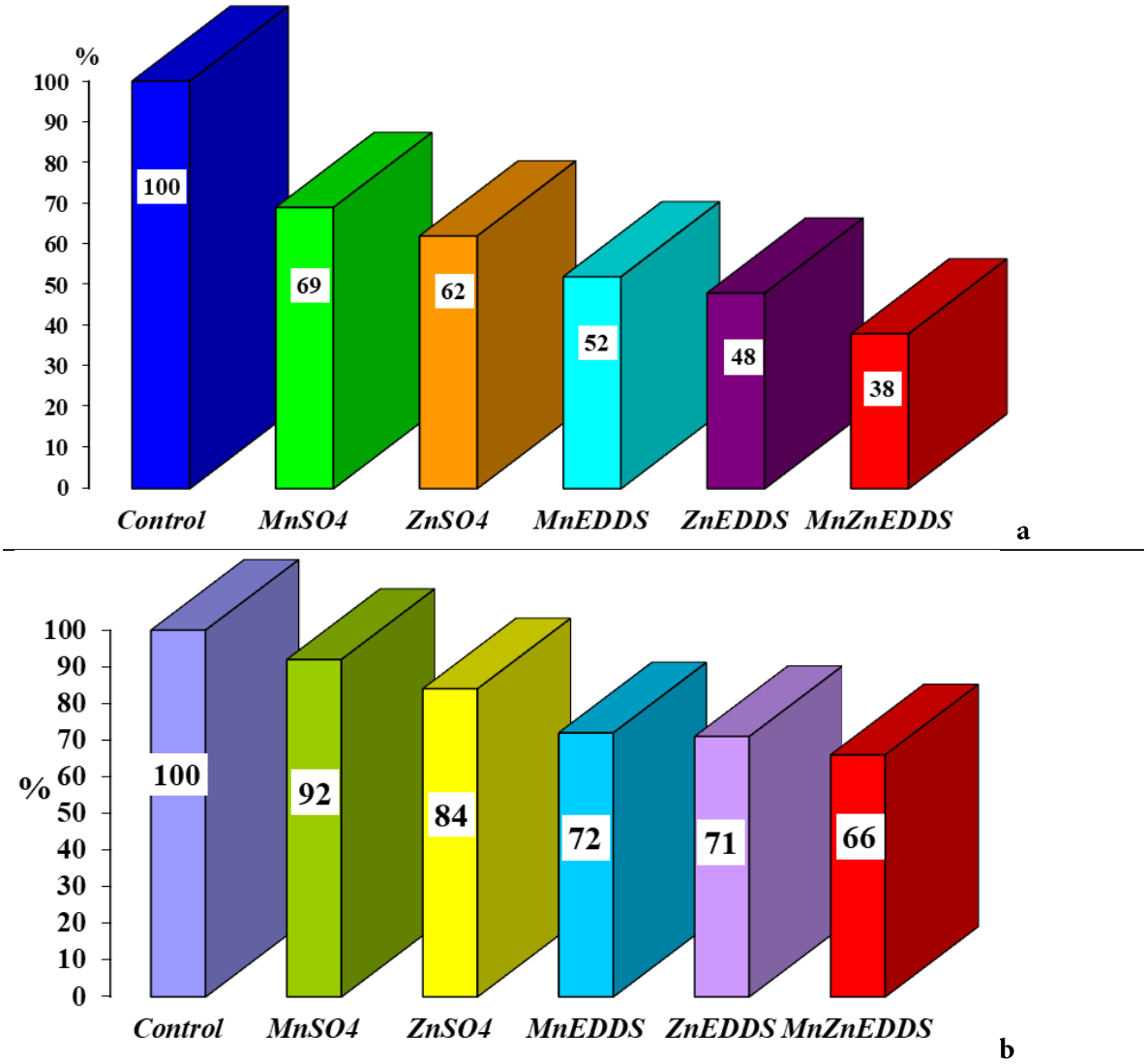


Fig. 14 – Influence of microelements and their complexonates on the accumulation of ^{137}Cs and ^{90}Sr in the lupine vegetative mass.

The obtained results confirm the opinion that one of the mechanisms of reducing the accumulation of ^{137}Cs and ^{90}Sr by plants under the influence of microelements can be due to the antagonistic interactions of microelements and the radionuclide on the one hand, and on the other hand, to an indirect effect due to the stimulation of the entry of macroelements into plants – its antagonists , in particular potassium, calcium and possibly some other elements, a noticeable increase in the amount of which in plants was found during foliar treatments with zinc, cobalt and manganese. It is likely that the effect of the use of complexonates is associated with better penetration of the trace element through cell membranes, the ability to be di-

rectly incorporated into the molecular structures of enzymatic systems, bypassing many transport chains.

CONCLUSIONS. The role of trace elements in plant nutrition is multifaceted. In particular, Cu, Mo, Mn, Co, Zn, B and others increase the activity of many enzymes and enzyme systems in the plant body and improve the plant's use of nutrients from the soil and fertilizers. Therefore, trace elements cannot be replaced by other substances, and their deficiency must be filled. Only then will we receive high-quality products that contain the optimal amount of sugars, amino acids, and vitamins for this variety. Microelements can accelerate plant development and seed ripening. They increase the resistance of plants to adverse environmental conditions (lack of moisture in the soil, increase or decrease in temperature). In addition, they protect plants from a number of bacterial and fungal diseases (bacteriosis of flax, beet heart rot, gray spotting of cereals, etc.), but unlike the effect of toxic chemicals, this occurs due to an increase in plant immunity.

The scientifically justified use of microelements in agricultural production is based not only on the need for them of a certain crop, but to a greater extent on their retention in the soil. It was established that the content of trace elements in the soil determines their content in plants, affecting their productivity and the quality of the yield. In this regard, the basis for the development of measures for the production and use of microfertilizers should be the content of microelements in the soil, their geographical distribution and distribution along the soil profile.

It has been established that trace elements in the form of inorganic salts work satisfactorily only in acidic soils. In soils close to neutral, their effectiveness decreases tenfold. In neutral, weakly alkaline and carbonate soils, inorganic salts cannot retain microelements in a water-soluble form available to plants and their efficiency approaches zero, i.e. they turn into poorly soluble forms (hydroxide, carbonates) and become unavailable to plants.

The researches of agrarian scientists and chemical scientists established that microelements are most effective for plants in the form of metal complexes (chelates). In particular, the complexes are stable in all types of soil and there are no soil pH restrictions for them. It should be noted that the specific properties of various soils and the complex physiological processes occurring in the plant have a noticeable effect on the action of complex compounds. In this regard, it is difficult to assume the possibility of creating a universal means of combating the lack of trace elements on various soils. The most reliable solution to this problem is the creation of a wide range of metal chelates for their differentiated application depending on the nature of the plant and the nature of the soil.

In addition, the use of microelement complexes can be an effective additional measure to reduce the ingress of radionuclides into agricultural plants, especially in biogeochemical provinces with their deficiency.

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РОЛЬ ХЕЛАТНИХ КООРДИНАЦІЙНИХ СПОЛУК БІОГЕННИХ МЕТАЛІВ У ЖИТТЄДІЯЛЬНОСТІ РОСЛИН

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В оглядовій статті розглянуто основні питання створення та застосування сучасних хелатних мікродобрив на основі мікроелементів у сільськогосподарському виробництві. Висвітлено питання ролі мікроелементів у життєдіяльності живих організмів та способи подолання нестачі мікроелементів у рослинах. Представлено огляд координаційних сполук 3d-металів (Fe, Mn, Zn, Cu, Co, Ni, Mo) з різними класами комплексонів, особливості їхньої будови та властивостей. Міститься актуальний матеріал про використання комплексонатів мікроелементів для створення сучасних хелатних добрив. Приділено увагу застосуванню комплексонатів мікроелементів на забруднених радіонуклідами (^{137}Cs, ^{90}Sr) територіях.

Ключові слова: координаційні сполуки, мікроелементи, хелати, комплексони, добрива, рослини.

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