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SMARAGD AS NEW CHELATED-GUMATIC PREPARATION FOR IMPROVING THE ENVIRONMENTAL STATE OF THE SOIL - PLANT SYSTEM

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Abstract

A new method of obtaining fertilizer and soil improver and the procedure for using the chelated-gumatic drug Smaragd with a fertilizing-stimulating and remedial effect have been substantiated and elaborated. The method aims to improve the ecological condition and increase the stability of the soil-plant system due to the creation and use of a new effective composition of the drug. New composition ensures the saturation of the soil with trace elements in a form accessible to plants, increasing plant productivity, including under conditions of heavy metal pollution, arid conditions on carbonate and eroded soils for simplifying the preparation and use of the drug and simultaneously saving resources. The new chelated-gumatic preparation of the proposed complex composition contains trace elements (Fe, Mn, Zn, Cu, Co, Mo and B) in the form of chelate compounds; the gumatic component of the composition is of natural origin. The agents of the new drug Smaragd interact in a certain ratio. The method is protected by a security document (utility model patent 135145 UA 2019).

***Key words**: Smaragd chelated-gumatic preparation, soil-plant system, remediation, microbiological and biochemical activity of soil, trace elements, heavy metals pollution.*

INTRODUCTION

Improving the ecological state of the soil-plant system by optimizing the plants mineral nutrition using the effect of humic acid, chelates, nano-chelates on the absorption of nutrients, grain yield (Najafi et al., 2020; Hayati et al., 2022) and the remediation of the polluted soil-plant system under the heavy metals (HM) contamination influence (Kumar et al., 2022; Damian et al., 2019; Samokhvalova, 2017; 2018) are an urgent, multifaceted and complex problems to solve today.

A special place among remediation activities is occupied by effective compositions of preparations, which contain biologically active chelated compounds of trace elements (TE) together with humates, which bind and reduce the chemical activity of various natures pollutants and prevent their migration from the soil to adjacent environments. Such specific properties of drugs chelate-humate compositions and complexes support their further use. Their ability to biodegrade pollutants (complete mineralization, minimal ecological «footprint») in the trophic chain - soil-plant-animal-human is important. TE is used by all living organisms in small quantities, however, their structural and functional role is significant due to the participation of TE in the transformation processes of substances and energy into biological (microorganisms, plants, animals, humans) and bioinert (soil, silt, weathering crusts; sea, river and lake water, etc.) systems. Each of the TEs performs strictly certain functions and cannot be replaced by another element. The use of TE is an important condition for increasing the production and quality of agrophytocenoses products, because the removal of nutrients (macroelements N, P, K; TE - Mo, Zn, Fe, Co, Mn, Cu, I, B, etc.) from the soil increases with the growth of plant productivity, the balance of nutrients is disturbed. Lack or excess of TE certain in plant products and feed can cause human and animal diseases. Therefore, TE is included in microfertilizers (inorganic compounds; frits; synthetic chelates and organic complexes; nanomicrofertilizers), which differ significantly in properties (physical state, chemical activity) and availability of the active substance for plants.

It was established (Bulygin et al., 1999), that from a biological point of view, ethylenediaminetetraacetic acid (EDTA) is a promising complexone for the creation of microfertilizers with the aim of soil introducing to replenish the lack of TE that affect the quality of agricultural products. However, until now, it is impossible to give an unequivocal answer to the question of which of the known complexones (EDTA, DTPA, OEDF, etc.) should be used to obtain biologically active TEs.

The main role belongs to the metal, and the complexion plays the role of a "vehicle" that ensures the delivery of the cation and its stability in the soil and applied nutrient solutions. Complexones determine the effectiveness of microfertilizer, which is determined by the degree of absorption of TE by plants.

In addition, the production of chelated microfertilizers is high-tech and knowledge-intensive. The tasks of elaborating new preparations containing TE chelates with the effects of fertilizer and stimulation of plant growth are being updated. In addition, the properties of complexones and complexonates based on them should be taken into account.

An important, complex and still unresolved issue for producers, as well as for consumers of chelated microfertilizers in Ukraine, is the degree of TE chelation, as an indicator of the predicted manifestation of microfertilizer effectiveness. In Europe, this indicator is fixed in the EU Directive 2003/2003 and is at least 80% (Regulation EC, 2003). There are no such regulatory documents in Ukraine.

Thus, the use of complexons and preparations based on them has a spectrum of application limitations, which should be taken into account both in the elaboration of chelated microfertilizers, chelated-humate preparations and in the practice of their use under background conditions and the influence of man-made pollution.

The presence of the listed imperfections requires the further elaboration of new highly effective, balanced in composition, complex preparations of fertilizing action, which are effective in the soil-plant system, in order to increase productivity under background conditions and improve its ecological condition under the pollution influence.

Exploring and exploiting soil improvers with a high adsorption capacity and low cost should be an effective method for overcoming the remediation problem HM pollution of soil-plant system.

The purpose of the research is to elaborate a method of obtaining a chelate-humate drug with a fertilizing-stimulating and remedial effect to improve the ecological state of the soil-plant system due to: (1) creating and using a new effective composition of the drug that ensures soil saturation with TE in a plant-available form, increasing the productivity of plants, including under conditions of pollution by heavy metals (HM); (2) simplification of obtaining and using the drug while saving resources.

MATERIALS AND METHODS

The method elaboration included expertise in conducting scientific researches, namely:

1. *Stage of informational and analytical research*. Analysis of methodical approaches to the elaboration of new chelate-humate preparations, including under the conditions of man-made pollution of HM; conducting a patent search (DSTU 3574 and DSTU 3575, 1998) and forming a working idea (hypothesis). Researched objects: available sources of scientific information (catalogues of periodicals, card files of articles and reviews using information and search systems, databases and data banks, the Internet), including databases of scientific and technical information on copyright objects that are patented in Ukraine and the countries of the post-Soviet space and EU, in context of the goal with an emphasis on the stages of known technical solutions, methods of obtaining them and fields of application. Research methods - methods of theoretical analysis, systematic approach.

2. *The stage of exploratory and field research.* Conducting exploratory researches in 2012 - 2014, microfield experiments (MFE) in the

natural-climatic zone of the forest-steppe (Sumy region) and steppe (Donetsk region) of Ukraine during 2014 - 2016, including taking into account soil contamination of the HM for the approval of a new Smaragd chelate-humate preparation (CGP). The experiments were carried out in accordance with the field experiment method (Dospekhov, 1985). The objects of the study are individual indicators of microbiological and enzymatic activity of different types of soils, the content of TE /HM (Cu, Co, Mn, Fe, Zn, Ni, Cr, Cd, Pb) mobile forms in the soil-plant system, the new Smaragd CGP, test plants (productivity, elemental composition).

The fertilizing-stimulating and remedial effect of Smaragd CGP using and the improvement of the soil-plant system ecological state was established by conducting MFE on the chernozem typical medium-loam of research ground within the Okhtyrka city, Sumy region; including under the influence of mono - and multi-metal Cd, Pb, Zn, Ni pollution. The test cultures - *Hordeum vulgare* L., *Lupinus angustifolius* L. The spectrum and levels of soil pollution of the HM correspond to the existing levels of pollution around PJSC "Sumikhimprom", where the excesses of the background content of Cd and Ni in the soil we established differs in 4 and 6 times, respectively; Pb and Zn - in 8 times.

Scheme of the experiment (12 variants, performed in triplicate): (1) Control; (2) Control + Smaragd CGP; (3) Cd soil pollution (4 background) + Smaragd CGP; (4) Cd soil pollution (4 backgrounds); (5) Pb soil pollution (8 backgrounds) + Smaragd CGP; (6) Pb soil pollution (8 backgrounds); (7) Zn soil pollution (8 backgrounds) + Smaragd CGP; (8) Zn soil pollution (8 backgrounds); (9) Ni soil pollution (6 backgrounds) + Smaragd CGP; (10) Ni soil pollution (6 backgrounds); (11) ∑HM pollution + Smaragd CGP; (12) ∑HM pollution.

Smaragd CGP was applied to the soil before sowing the test plants in a specified dose of 2.5-3 l/ha and 1.5-2 l/t - for seed treatment; 2.5-3 l/ha - for feeding plants in the phase of their active growth and development, with doubling of the drug applied doses for Cd, Pb, Ni, Zn multi-metal soil contamination.

Approbation of the Smaragd CGP was also carried out in field studies on chernozems ordinary of the Steppe zone of Ukraine (laboratory of soil fertility and soil protection technologies of the State Enterprise "Donetsk" NSC "IGA named after O.N. Sokolovsky"). Scheme of the field experiment (3 variants, performed in triplicate): (1) Control; (2) Reacom, 3 l /ha; (3) Smaragd CGP, 3 l /ha. The registered area of the trial plot is 25 m^2. The test crop - *Helianthus annuus* L. The effectiveness of foliar treatment of sunflower crops in the 12-leaf phase was studied.

The selection of soils samples from the arable (up to 20 cm) layer was carried out in accordance with the current regulatory documents - DSTU 4287:2004; DSTU ISO10381-6:2001. Selection of plant samples and their mineralization with the GOST 27262-87 and DSTU 7670:2014. All measurements were performed in triplicate.

3. *The stage of soils and plants samples chemical-analytical and laboratory researches*.

Determination of the orientation and intensity of individual microbiological and biochemical soil processes under the conditions of application of the new Smaragd CGP was carried out by analyzing soil samples in the Department of Soil Protection and the Sector of Soil Microbiology of the NSC "IGA named after O.N. Sokolovsky", according to the current regulatory documents and methodical base.

The following indicators of biological properties were determined in the soil samples: the number of microorganisms of the main ecological and trophic groups was determined by the method of microbiological sowing (by the deep method) of the soil suspension of the appropriate dilution on solid nutrient and liquid nutrient media (DSTU 7847:2015). Biochemical activity of soils was determined by the polyphenoloxidase activity (Karyagina and Mikhailovsky, 1986).

Atomic absorption determination of the TE/HM (Mn, Zn, Cd, Co, Ni, Fe, Pb, Cu, Cr) mobile forms content in soils and plants (DSTU 4770.1:2009 - DSTU 4770.9:2009; DSTU 7607:2015, DSTU 7831:2015, Methods of soil and plant analysis, 1999).

Determination of the cation-anion composition of water samples was carried out with current regulatory documents (DSTU 7525:2014; DSTU

7908:2015; DSTU 7909:2015; DSTU 7943:2015; DSTU 7944:2015; DSTU 7945:2015).

4. *Stage of chamber studies.* Establishing structural relations of soils biological and chemical properties based on the information estimation of the TE status of soils by means of expert evaluation of normative and reference documentation, conducting calculations of indicators of microbiological and enzymatic activity of the soil; statistical processing of the received data, including under the influence of HM man-made pollution; use of mathematical and statistical methods. Statistical processing of the received numerical data was carried out using the *Statistica* 10.0 software. Differences in average indicators were considered reliable at the significance level of $p<0.05$. *Microsoft Excel* 10.0 software was used to visualize the obtained data.

The assessment of the elemental status of the test plants was carried out in accordance with the current maximum permissible levels (MPL) of the chemical elements content in animal feed (Methodological guidelines, 1998). The assessment of the microelement status was carried out using the established background levels of TE content for the soils of natural and climatic zones of Ukraine (Fateev and Samokhvalova, 2012).

RESULTS AND DISCUSSIONS

Based on the results of long-term exploratory chemical-analytical and field researches in 2012-2016, we established the following: (1) conditions and components suitable for joint use, which promote the creation of new complex balanced fertilizer preparations that increase the synergistic effect of TE chelates (Fe, Mn, Zn, Cu, Co, Mo, B) using, where the chelating substance is oxyethylidenediphosphonic (OEDF), and humates in the established ratios of their concentrations, which ensure a high rate of their absorption by plants; (2) stability of the chelate-humate composition solution and the possibility of its further use in a wide range of component ratios, independence from water hardness; (3) increasing the efficiency of using chelated microfertilizers, in particular on carbonate and eroded soils; (4) fertilizing and stimulating effects of a wide range of chelate-humate composition ratios for the plants on soils of various types, the functioning of the soil-plant system as a whole, including the remedial effect under the conditions of mono- and polyelement technogenic soil pollution.

Due to the analysis of the existing patent documentation regarding to the subject of research, there have been established methods-analogues, which contain defined algorithms for obtaining and using new drugs. In particular, the well-known method of obtaining microfertilizers (Patent 64773 UA, 2004) involves the use of TE (Zn, Cu, Fe, Mn, Co, Mo, B) and complexone containing either carboxyl groups of one of the acids of the polyaminopolyacetic group (the most common ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), etc.) or phosphonic groups of one of the acids of the alkyd phosphonic group (the most common of them are OEDF, etc.) and the introduction of complexone of polybasic organic acid (in particular citric) in the ratio of complexons based on carboxyl or phosphonic groups of 50-80%, polybasic organic citric acid - 20-50 %, which increases the efficiency of microfertilizer nutrient absorption by plants several times compared to soluble mineral salts.

However, the use of artificial complexons of the III and IV hazard classes has limitations, including due to the high probability of their destruction under the influence of ultraviolet light, biodegradation and toxicity of the products of their transformation for plants and soil microorganisms (Williams, 1975; Dyatlova, 1988; Nanda, 2016), increased risks of soil pollution and groundwater, fixing of metals in the DNA of living organisms (Kasyanenko, 1989; Paston et al., 2016).

We established that the method of obtaining microfertilizer with a complex of biostimulators Yaramiks (Patent 75452 UA, 2012) involves obtaining a microfertilizer containing an aqueous solution of N, K, S salts and Fe, Mn, Cu, Zn, B, Mo, Mg, Co chelates; succinates, tartrates, citrates; lithium ions, complex lignosulfonates (LST), which are structurally similar to soil fulvic acids. However, given the established effectiveness of LST, their main drawback is the instability of the structure and functional groups, which requires the addition of compounds with oxidizing properties (nitrites, nitrates, etc.) and/or complexing agents - Cr (VI), Fe (III), Al (III), and/or organic compounds of alkaline reagents for LST stabilization, which leads to additional costs of resources and an increase in the cost of fertilizer.

We discovered the method of obtaining microfertilizer with a complex of biostimulators Nanomix (Patent 61566 UA, 2011) involves obtaining a microfertilizer with a complex of biostimulators, which contains an aqueous solution in a certain ratio of components - salts of N, K, S and Fe, Mn, Cu, Zn, B, Mo, Mg chelates; succinates, malates, tartrates, citrates, Co chelates and additional substances (growth stimulants - β-indolylacetic acid and/or β-indolylbutyric acid; polyvinyl alcohol, water); chelates based on OEDF, EDTA, ethylenediamine-disuccinic (EDDS), succinic, malic, tartaric and citric acids.

Obtaining microfertilizer is expensive due to the use of a wide nomenclature of specific fertilizer components, artificial complexes. Succinic, malic, tartaric, and citric acids are weak chelating agents for Zn, Cu, and Fe, with substitution in the soil solution and root zone of TE plants by calcium, which leads to a significant decrease in fertilizer efficiency and coagulation with humates.

In addition, based on the results of chemical-analytical studies, we established the incompatibility (coagulation) of TE preparations, in particular Nanomix fertilizers with alkali metal humates, which makes them limitedly suitable for use in compositions with this organic fertilizer and on alkaline soils.

The closest in composition and balance to the proposed complex chelate-humate preparation is the soluble organo-mineral fertilizer based on the organic fertilizer Biocycle-1 (Patent 86907 UA, 2009), which was obtained by extraction with alkaline reagents of the organic fertilizer Biocycle with a predominance of humates followed by the dissolution of organo-mineral components (urea, monosubstituted or disubstituted, or trisubstituted potassium phosphate, macroelements Mg and Ca; TE (Fe-Mn-Zn-Cu-Co) in the form of chelating salts, where the chelating substance is EDTA salt or its analogues, B and Mo, in the form of boric acid and sodium or ammonium molybdate; a mixture of polyethyleneglycols (PEG), plant growth regulators for processing seeds and vegetative mass of plants.

However, the analogue method is characterized by the high cost of obtaining fertilizer due to the need to involve modern equipment, significant doses of components for obtaining both new fertilizer and the organic-mineral fertilizer itself. In addition, it is known that Mo and B in the composition of acids and salts are in the anionic form, which is characterized by a low level of assimilation by plants from the soil and does not form chelate complexes, comparable to cations of polyvalent metals. This creates difficulties in the fixation of Mo and B in water-soluble compounds, which are eliminated by the introduction of PEG, which are characterized by the transformation into a soluble state of difficult or insoluble components of the drug, increased absorption of substances, convenience and accuracy of dosing. Still, the main disadvantage of PEG solutions is the complexity of preparation and stabilization, large volume and the need to use special containers, etc. In addition, the organic component of the fertilizer is up to 70%, chelate - up to 3%, which leads to an increase in the risk of coagulation due to an increase in the content of the chelate component. Such an imbalance in the composition determines the introduction of more effective complexons in order to form of stable complexes with Mo, B.

Besides, the EDTA complex, which is used, is an unstable compound to the action of soil microorganisms and is capable of forming toxic hydrolysis products. EDTA-based TE chelates are restricted for use on soils with pH>7.5. For each element, stable compounds are formed only at certain pH values. The result of which is an increase in the risks of violation of ecological conditions in the root layer of the soil, a decrease in the biological and ecological safety of organo-mineral fertilizer, the efficiency of its use and the TE assimilation by plants.

Growth stimulators and regulators, as a component of the organic-mineral fertilizer based on Biocycle-1, belong to the 3rd and 4th class of danger; their specific effect on plants has not been sufficiently studied. The use of stimulators and growth regulators must be strictly regulated. According to the EU directive

2003/2003 of 13.10.2003, mandatory registration is provided for in the relevant state bodies separately for each country. Taking into account the fact that the majority of artificially synthesized specific growth stimulators are prohibited for application in agriculture, which significantly increases the risks of reducing the biological and ecological safety of fertilizer use.

In addition, the use of stimulators and growth regulators together with fertilizers requires highly qualified specialists, which increases the resource consumption of the method.

The elaborated algorithm of our proposed method includes the stage of obtaining and using Smaragd CGP:

1. *Preparation of Smaragd CGP* with fertilizing-stimulating and remedial action using a composition of chelate and humate components based on mixing their aqueous solutions. Soluble organo-mineral components containing TE in the form of chelated compounds using complexone, with additional introduction of Mo and B in the form of ammonium molybdate and boric acid to the chelated component of the preparation in the amount of 0.25-1.5 g/l and 10-20 g/l according to the established ratios of concentrations of other MEs chelates - Fe - 12-25 g/l; Mn - 15-25 g/l; Zn - 10-25 g/l; Cu - 5-10 g/l; Co - 0.15-2 g/l.

OEDF is used as a complexone in a stoichiometric amount with TE salts under constant stirring and pH control of the environment, followed by the introduction of a solution of known humate from organic raw materials of natural origin into the chelating component of the preparation, as an environmentally safe metal chelator. At the same time, the chelate and humate components of the composition interact in a ratio of 5:1-1:5, which makes it possible to obtain a water-soluble, liquid fertilizer Smaragd of the chelate-humate composition, balanced in terms of the TE content and humic substances.

As a chelating component of the drug, a solution of TE chelates used in the established ratios of active substances concentrations and OEDF at pH 5.4-7.5 for maximum assimilation of nutrients by plants.

In particular, to obtain 30 liters of the chelate component of the drug containing TE, aqueous solutions of their compounds are prepared by dissolving them in water in a volume sufficient for their complete dissolution, taking into account the established reference values of the product of their solubility. Seven containers are used, respectively, to dissolve iron chloride (III) ($FeCl_3x6H_2O$) - 1.92 kg; manganese sulfate ($MnSO_4xH_2O$) - 1.23 kg; zinc sulfate ($ZnSO_4x7H_2O$) - 1.75 kg, copper sulfate ($CuSO_4x5H_2O$) - 0.64 kg; cobalt sulfate ($CoSO_4x7H_2O$) - 0.15 kg; ammonium molybdate $(NH_4)_2MoO_4$ - 0.02 kg; boric acid (H_3BO_3) - 1.68 kg. Next, TE chelation is carried out by adding OEDF complexone in the form of powder, respectively 1.5 kg - 1.5 kg - 1.4 kg - 0.54 kg - 1.5 kg - 0.15 kg - 2.9 kg to each of the seven containers with ready-made aqueous solutions of TE with constant stirring and control of the pH of the medium with subsequent mixing of the obtained aqueous solutions of TE chelates into one.

By adding potassium hydroxide or potassium carbonate, the pH of the resulting solution of chelate compounds is adjusted to 4-7 units as needed. In this way, the chelating component of the Smaragd drug is obtained. The volume of its solution is brought up to 30 liters by adding water followed by filtering.

As a humate component of Smaragd drug, which contains low-molecular complexes with organic acids easily absorbed by plants, a solution of any available humate from organic raw materials of natural origin is used. For example, potassium humate extracted from peat with a humic acid content of 18.7 g/l; fulvic acid content - 8.8 g/l; pH - 9.7. In the solution of the chelate component of the drug in the amount of 30 liters, added a solution of potassium humate in the amount of 10 liters and we get the composition of the fertilizing Smaragd CGP with a high buffer capacity. In the combination of active agents of the proposed composition, water-soluble complexes of organic acids with multivalent metals are formed. The volume of the obtained concentrate is 40 liters; it is additionally filtered and packaged in a plastic container. The elaborated fertilizer Smaragd CGP is a homogeneous liquid of dark brown color with a pH of 6.5-7.5.

2. *Approbation of the new Smaragd CGP* by using the obtained preparation for pre-sowing treatment of seeds at a dose of 1.5-2 l/t and vegetative mass of plants at a dose of 2.5-3 l/ha with an increase in their productivity and adaptogenic properties, and introduction into the soil in a dose of 2.5-3 l/ha, and for multi-metal soil contamination with Cd, Pb, Ni, Zn by doubling the doses of the drug.

The effectiveness of the Smaragd CGP use to improve the ecological state of the soil-plant system by enhancing ecological functions (trophic, protective) was confirmed by an increase in the content of ecological-trophic groups - fungi, nitrogenfixers, and biochemical activity of the soil (Figures 1-3) according to the indicator, for example, polyphenol oxidase activity, productivity of test plants (Figures 4-6).

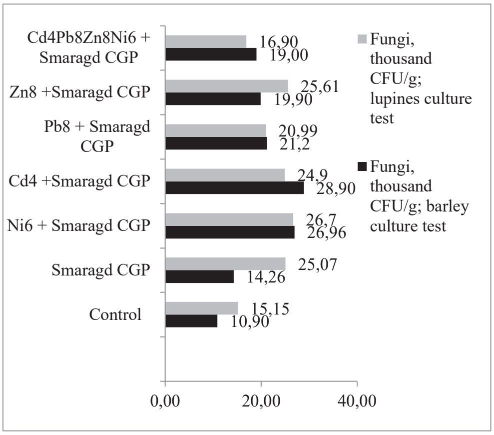


Figure 1. The influence of the Smaragd CGP use on the content of fungi in soil taking into account the test plants

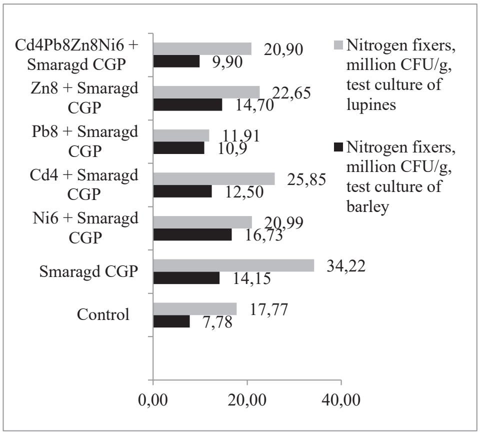


Figure 2. The influence of the Smaragd CGP use on the content of nitrogenfixers in soil taking into account the test plants

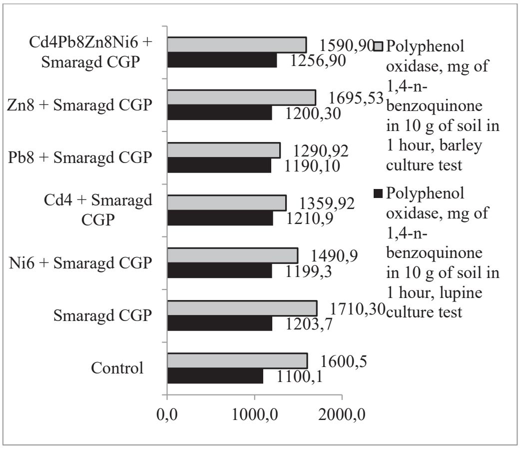


Figure 3. The influence of the Smaragd CGP on the biochemical activity of the soil taking into account the test plants

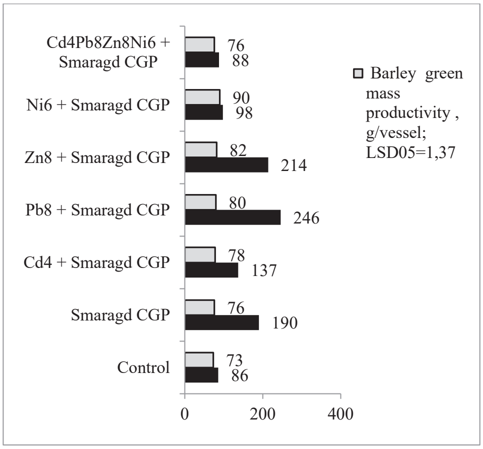


Figure 4. The influence of the Smaragd CGP on the productivity indicators of the green mass of the test plants

In particular, it was established that the Smaragd CGP introduction within the specified time period increased the productivity of grain, green mass and the root system of barley - by 21% and 4% and 2 times; lupine - the increase was 5 and 2.2 times, respectively, and by 46.6%. The Smaragd drug had a positive effect on the development of vegetative and generative organs of plants grown under soil monoelemental pollution with Cd, Pb, Zn, Ni (Figures 4-6). The effectiveness of the Smaragd drug was discovered and confirmed on Zn and Ni contaminated soil with the strengthening of the fertilizing and stimulating effect, increasing the adaptogenicity of plants and the productivity of green mass, grain and stimulating the development of the root system of test crops (Figures 4-6).

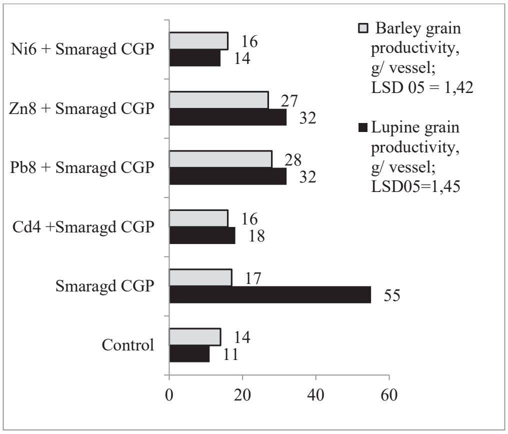


Figure 5. The influence of the Smaragd CGP on the productivity indicators of the grain of the test plants *Hordeum vulgare* L. and *Lupinus angustifolius* L.

[1]LSD $_{0.05}$ - Least Significant Difference at p = 0.05 in Figures 4-6.

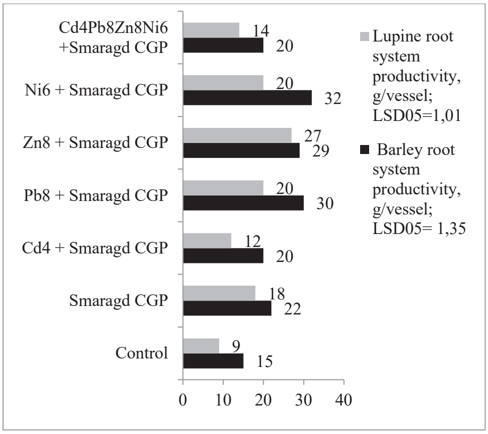


Figure 6. The influence of the Smaragd CGP on the roots system productivity of the *Hordeum vulgare* L. and *Lupinus angustifolius* L.

On MFE variants under the influence of soil HM multi-metal contamination, the use of the Smaragd CGP in the soil and foliar feeding of plants and pre-sowing treatment of seeds, a positive effect was obtained with an increase in the productivity of the green mass of lupine and barley by 2.3% and 4%, the root system - by 33% and 1.6 times, respectively. It was established that the saturation of the contaminated soil of TE with the introduction of Smaragd CHP leads to an increase in the content of mobile forms of Co, Cu (Figure 7), which ensures a decrease in the toxicity of Cd (Figure 8) in the soil-plant system, improvement of its ecological condition as a result of a certain optimization of the elemental status of the soil and the test plants - *Hordeum vulgare* L. and *Lupinus angustifolius*.

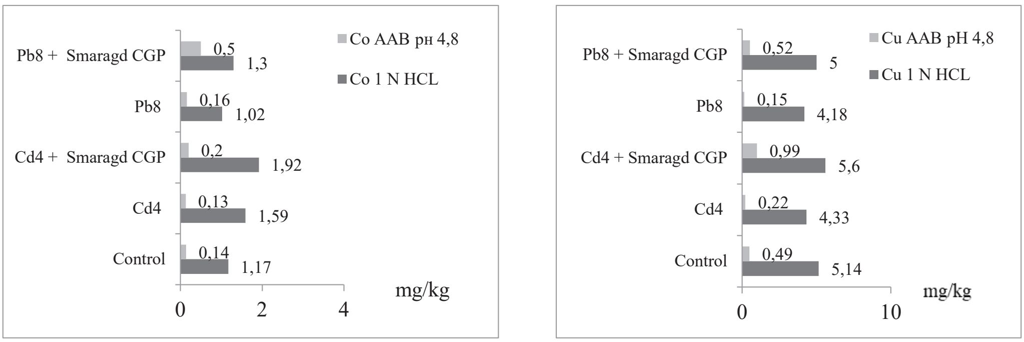
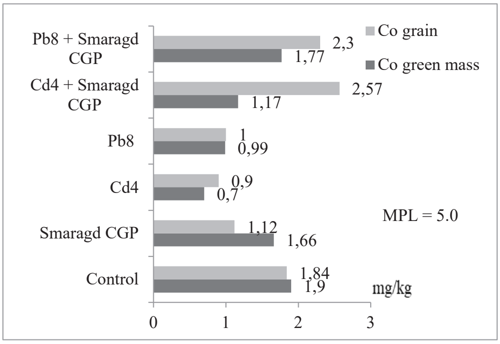


Figure. 7. The effect of the Smaragd drug use for the optimization of the elemental status of the soil

CHP Smaragd promotes the growth of ME content in barley test plants.

In particular, the accumulation of Co (Figure 8) and Fe increased 1.7 and 1.2 times in the vegetative mass and 2 times in barley grain for a decrease of 2 times or more in the content of the toxic metal Cd (Figure 8). A 1.7-fold increase in the content of Cu in barley grains was established, which proves the existing adaptogenic properties of the drug due to its influence on the optimization of the TE composition of test plants under conditions of HM soil contamination.



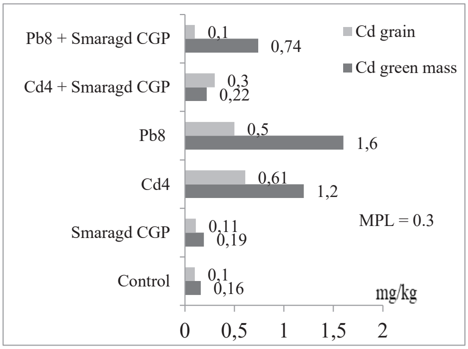


Figure. 8. The effect of the Smaragd drug use for the optimization of the elemental status of the test plants *Hordeum vulgare* L.

Thus, due to its fertilizing and growth-stimulating properties, Smaragd CGP contributes to the improvement of the ecological condition of plants with an increase in yield.

The Smaragd CGP does not have a limit on water hardness, compared to the existing ones. Data on the suitability of water of different hardness, with the established chemical analysis of the mineral composition, are given in Table 1. When using solutions of the components of the Smaragd CGP composition, the absence of coagulation due to excess calcium and magnesium in the water was recorded.

Approbation of the proposed Smaragd CGP in field studies on chernozems ordinary (DP DG "Donetsk") showed an increase in yield during foliar fertilization of sunflower (*Helianthus annuus* L.) in the phase of 12 pairs of leaves (Table 2), in contrast to the action of the drug Reakom, which forms insoluble complexes with calcium.

Table 1. Results of a standard chemical analysis of the mineral composition of different hardness water

Defined indicators	Current regulations according to DSaNPiN 2.2.4-171-10	Water sampling points for conducting experiments			
		Babai, Kharkiv region	Chuguiv, Kharkiv Region	Kharkiv, st. Otakara Yarosh, Sarzhyn Yar	Kharkiv, Florinka
pH	6.5-8.5	6.81	6.63	7.07	6.56
CO_2, mg/l	-	66.0	92.4	96.8	8.8
HCO_3^-, m-mol /l		7.2	7.8	3.9	10.2
Cl^- residual bound, m-mol /l	≤1.2	6.8	1.8	4.0	1.6
SO_4^-, m-mol /l	≤250	4.28	13.88	5.79	9.5
∑ anions, m-mol /l	-	18.28	23.48	13.69	21.3
∑ Ca^{2+}+ Mg^{2+}, m-mol /l	7-10	18.0	22.6	10.8	20.6
Ca^{2+}, m-mol /l	25-75	10.4	19.5	6.6	16.6
Mg^{2+}, m-mol /l	10-50	7.6	4.8	4.2	2.0
∑ Na^++ K^+, m-mol /l	-	0.28	0.88	2.89	0.7

Table 2. The effect of various drugs on the biological yield of the test plant in the conditions of the Steppe

Variant	Biological yield of sunflower (*Helianthus annuus* L.), soil - Chernozem ordinary (data table fragment)	
	t/ha	Increase, t/ha
Control	24.1	–
Reacom preparation, 3 l/ha	26.4	2.3
The Smaragd CGP, 3 l/ha	29.2	5.1
$LSD_{0.05}$	3.6	–

[1]LSD 0.05 - Least Significant Difference at p=0.05

Due to the proposed composition of Smaragd CGP, the occurrence of calcium coagulation is eliminated, both in soils and in plants; an increase in their effective action with OEDF during the period of agrophytocenoses cultures active vegetation is ensured, which was confirmed by an increase in the productivity and adaptogenicity of plants, taking into account the unfavorable conditions of increased carbonation and soil erosion (depletion of biogenic elements reserves in particular N, P and the content of mobile forms of TE in soils (Fe - 2 times, Zn - 3 times, Co and Cu - 5 times) according to the drug-induced resistance of plants to arid conditions during the test period.

Furthermore, according to the observations results of the meteorological indicators dynamics during field researches on the approbation of the Smaragd CGP action (Table 3), stable trends to an increase in the temperature background and a seasonal redistribution of the amount of precipitation with an increase in dry manifestations of the period of agrophytocenoses crops active vegetation were established (Pogromska, 2018). Our data confirmed the positive trend of regional changes in the number and intensity of extreme weather events (rainfall, average wind speed, intensity and frequency of storms, etc.) (Project Report, 2014).

The elaborated algorithms for the creation and use of the Smaragd CGP to improve the ecological state of the soil-plant system are protected by utility model patent 135145 UA, 2019. The elaboration refers to the methods and technologies of obtaining fertilizers and soil conditioners and their use, including in the case of man-made pollution of the soil-plant system with heavy metals.

Table 3. Meteorological indicators at the Sukha Balka agrometeorological station, Yasynuvatsky district, Donetsk region

Year	Air temperature, ºC				Precipitation, mm				Soil surface temperature, °C			
	Months of the year											
	ІУ	У	УІ	УП	ІУ	У	УІ	УП	ІУ	У	УІ	УП
2010	10.6	18.4	24.1	26.5	32.0	95.0	59.0	40.5	14.4	22.7	31.3	31.6
2011	9.1	18.5	21.7	25.8	35.5	51.5	106.0	34.0	11.4	24.4	27.8	31.8
2012	14.6	20.4	23.0	25.6	26.0	66.5	88.0	17.5	17.7	25.9	29.4	30.8
2013	12.3	21.6	23.5	23.7	18.0	47.5	50.0	28.7	14.6	27.6	30.3	29.5
2014	10.4	19.5	19.9	24.3	27.0	85.5	95.5	76.5	13.9	22.4	23.8	27.6
2015	9.6	17.4	23.3	23.8	75.0	29.0	43.0	125.0	11.8	22.4	28.5	28.2
2016	15.1	19.6	25.9	29.9	40.0	87.0	39.5	8.5	14.4	18.6	24.0	28.1
2017	10.8	18.4	24.7	25.2	70.5	46.0	32.6	28.6	11.2	20.8	29.7	30.9
2018	14.5	20.7	24.5	25.5	20.8	25.9	40.7	88.4	15.0	22.6	27.5	27.0
1995 - 2005	10.8	17.5	21.5	24.3	43.8	41.6	91.4	64.2	12.9	21.6	27.4	30.2

A new method of improving the ecological state of the soil-plant system using the Smaragd CGP is advisable to use when growing plants in open and closed soil, hydroponics, under irrigation and fertigation conditions, pre-sowing incrustation of seed material, root and foliar feeding of plants in critical periods of their growth and development to increase quality and productivity levels and improve soil quality; as well as remediation of the soil-plant system HM contaminated, insufficient moisture on carbonate and eroded soils.

CONCLUSIONS

A new Smaragd CGP and an algorithm for its using on chernozem soils of the Forest-Steppe and Steppe zones of Ukraine were elaborated. Application of the algorithm ensures: (1) saturation of the soil with TE in a form available to plants; (2) improvement of adaptogenic properties with increased plant productivity; (3) improvement of the ecological state of the soil-plant system, including under conditions of soil pollution and arid conditions on carbonate and eroded soils due to the proposed effective composition of the drug, simplification of its preparation and use, and simultaneous resource conservation. The fertilizer is designed for pre-sowing seed treatment and plant feeding.

Distinctive properties and results of using the proposed Smaragd CGP, in comparison with known drugs, are as follows: (1) biological and ecological safety of the drug composition (quantitative and qualitative); (2) stability in a wide range of pH values of the environment, which ensures effective use of the drug on soils with a pH of 4.5-10 and increases its shelf life; (3) the preparation has no limitation on water hardness and is suitable for use in arid climatic conditions (high air and soil temperatures, minimization of precipitation); (4) the liquid form of the drug and the good solubility in water of the components of the proposed composition (metal complexes, gumatic component) enable consumers to obtain its working solutions in a wide range of chelated-gumatic ratios in the field in the necessary doses depending on the composition of the soil and the needs of the plants with simultaneous simplification of transportation and cheapening of its use; (5) the prolonged action of the drug, which is ensured due to the probable gradual release of TE from the drug regarding to the difference in the stability constants of metal chelates and the exchange capacity of fulvic and humic acids, as well as different solubility of complexes with a certain excess of OEDF complexone; (6) fertilizing and stimulating effect with the possibility of reducing the rates of introduction of components in terms of the active substance for its preparation and the rates of its application under plants and in the soil; (7) the remedial effect, ensuring the strengthening of the ecological (in particular, trophic, protective) functions of the soil and the improvement of the ecological state of the soil-plant system, including under the conditions of man-made HM pollution, arid conditions and on carbonate and eroded soils; (8) activation of growth processes of plants of various species and growth of their yield due to the mobilizing action of a natural components complex preparation.

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