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### ИЗМЕНЕНИЕ АКТИВНОСТИ КАТАЛАЗЫ И УРЕАЗЫ ПРИ ПОВЫШЕННЫХ СОДЕРЖАНИЯХ ТЯЖЕЛЫХ МЕТАЛЛОВ (Pb, Zn, Cd) В СЕРОЗЕМЕ

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В работе приведены экспериментальные данные по влиянию различных концентраций цинка, кадмия и свинца на активность каталазы и уреазы в сероземе. Изучалось влияние свинца (Pb) в дозах 25, 125, 251 мг/кг почвы, кадмия (Cd) – 0,6, 2,9, 5,9 мг/кг почвы, цинка (Zn) – 51, 254, 508 мг/кг почвы на ферментативную активность каталазы и уреазы при внесении в сероземную почву вермикомпоста и сероперлитсодержащего отхода и их смеси. Установлено увеличение активности каталазы и уреазы с повышением содержания свинца (Pb) в сероземном почве как без, так и в присутствии вермикомпоста, сероперлитсодержащего отхода и их смеси. Выявлено ингибирование ферментативной активности с увеличением содержания цинка (Zn) и кадмия (Cd) в почвенной системе. Данная закономерность сохраняется и при внесении в почвенную систему вермикомпоста, сероперлитсодержащего отхода. Как показали результаты, проведённых нами исследований, при внесении в сероземную почву интенсивное разложение перекиси водорода зависит от концентраций свинца, кадмия и цинка. С увеличением содержания исследованных металлов в почвенной системе наблюдается снижение активности каталазы и, соответственно, уменьшается скорость процесса разложения пероксида водорода.

**Ключевые слова:** тяжелые металлы, свинец, кадмий, цинк, активность уреазы, активность каталазы, серозем, вермикомпост, сероперлитсодержащий отход

### CHANGE OF CATALASE AND UREASE ACTIVITY AT HIGH CONTENT OF HEAVY METALS (PB, ZN, CD) IN SEROZEM

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The report presents experimental data on the effect of various concentrations of zinc, cadmium and lead on the activity of catalase and urease in serozem. The effect of lead in doses of 25, 125, 251 mg / kg of soil, cadmium – 0,6, 2,9, 5,9 mg / kg of soil, zinc – 51, 254, 508 mg / kg of soil on the enzymatic activity of catalase and urease in the use of vermicompost, sulfur-perlite-containing waste and mixtures thereof. An increase in the activity of the catalase and urease with increase in Pb content in the soil, both without and in the presence of vermicompost, sulfur-perlite containing waste and their mixture was determined. Inhibition of enzyme activity with increase in the content of zinc (Zn) and cadmium (Cd) in the soil system was revealed. This pattern is preserved at vermicompost, sulfur-perlite containing waste is applied into the soil system. As the results of our studies showed, when introduced into the gray earth soil, the intensive decomposition of hydrogen peroxide depends on the concentrations of lead, cadmium and zinc. With an increase in the content of the studied metals in the soil system, a decrease in the activity of catalase is observed and, accordingly, the rate of decomposition of hydrogen peroxide is reduced.

**Keywords:** heavy metals, lead, cadmium, zinc, activity urease, activity catalase, serozem, vermicompost, sulfur-perlite containing waste

As a result of the harmful anthropogenic effect on the soil cover, the total area of cultivated land resources is steadily being reduced from year to year [1], which may affect the degradation of the food supply of the Earth's population.

Biochemical soil homeostasis is supported by enzymes. Despite the significant heterogeneity of the soil, it maintains a relatively stable content of organic matter (humus, polysaccharides, amino acids, vitamins), the actual acidity characteristic of this type of soil, the content of mobile forms of elements, etc. [2]. The addition of mineral and organic fertilizers, pesticides, agricultural and industrial garbage

changes the biochemical balance of soils with a low content of enzymes and low biological activity. If the soil is rich in microorganisms, and if it has high enzymatic activity and buffering, the resulting changes fastly disappear, and the balance is recovered [2].

Being the most important biogeochemical barrier, the soil is exposed to the negative effects of heavy metals (HM) that fall into it as a result of the activities of industrial enterprises, the operation of vehicles, and the influx of municipal sewage. To date, HMs occupy leading positions in the scale of soil pollution, the consequence of which is a violation of their fertility. An important contribution to its

formation is made by soil enzymes participating in the processes of transformation of organic substances in the soil and providing living organisms with available nutrients. As is known, different types of soils respond differently to pollution. High buffering properties determine their best resistance to the effect of pollutants [1].

The reasons for the negative impact of HM on the biological properties of soils are that HM, binding to sulfohydryl groups of proteins, inhibit the synthesis of proteins, including enzymes, and change the permeability of biological membranes. Under the influence of HM, disturbances occur in the structure of soil microbiocenosis, which changes the level of enzymatic activity of the soil [3].

Immobilized (fixed on soil particles) enzymes in the soil are quite stable under conditions under which the microbiota's activity is suppressed, due to which the metabolism in the soil can remain relatively unchanged for a long time. Therefore, the value of enzymes in extreme conditions (high humidity, antibiotic drugs, pesticides, heavy metals) is especially high [4, 5].

Enzymatic activity can be used as an additional indicator of biological activity and soil fertility [6].

In the modern living world, up to a thousand enzymes are currently being discovered. It should be noted that all enzymes are found in the soil, but only for individual methods for their quantitative determination. The best methods have been developed for the determination of hydrolases (in particular, invertase, phosphatase, proteases, urease, amylases) and oxidoreductases (in particular, dehydrogenases, polyphenol oxidase, catalase) [7, 8].

The main role of hydrolases is their participation in the hydrolytic decomposition of high molecular weight organic compounds, that is, this type of enzyme plays an important role in the enrichment of the soil with mobile nutrients in a form accessible to plants and microorganisms [9, 10].

The action of the most common soil enzymes in soil contamination with heavy metals can help as an indicator of the degree of soil contamination. Moreover, such changes in enzyme activity serve as an indicator of early diagnosis of negative changes in soil properties [11].

*Catalase.* The most important soil enzyme from the class of oxidoreductases is catalase. It catalyzes the decomposition of hydrogen peroxide, which is formed during the respiration of plants and as a result of the biochemical oxidation of organic substances in soil, into water and molecular oxygen. Soil catalase activity is usually considered not

only as an indicator of the functional activity of microflora, but also the preservation of enzymes in post-mortal plant material [12]. The study of the relationship between the level of pollution and the maintenance of HM is one of the urgent tasks for using catalase as a bioindicator.

*Urease.* Urease is one of the most studied soil enzymes. It plays an important role in the conversion of soil nitrogen. The presence of urease in bacteria enables them to use urea as a source of ammonia, since urease catalyzes its hydrolysis [11].

Anthropogenic pressure on urban soils is also manifested in the influx of heavy metals into them due to the intensification of automobile traffic, the development of industry, and public utilities, which is one of the factors of soil degradation in urban conditions. But in addition to intracellular microbial urease, there is an extracellular urease in the soil adsorbed by soil colloids, which have a high affinity for it. Communication with soil colloids protects the enzyme from decomposition by microorganisms and contributes to its accumulation in the soil. Each soil has its own stable level of urease activity, determined by the ability of soil colloids, mainly organic, to exhibit protective properties [11].

The urease activity of the soil is characterized by the following characteristics: high information content (close correlation between the urease activity index and the anthropogenic factor), sufficiently high sensitivity, high specificity, good reproducibility of the results, slight variation, simplicity, low laboriousness, and high speed of the determination method. The most dangerous heavy metals include cadmium, lead, nickel, chromium, mercury, etc. [11]. Some metals vital for the mineral nutrition of plants are also classified as heavy (zinc, iron, copper), and at high concentrations they become dangerous [13].

An important role in the formation of soil fertility is played by soil enzymes. HMs inhibit their activity even in soils with high buffer capacity [13]. In this regard, it is of interest to study the activity of hydrolytic enzymes in anthropogenically modified soils.

The aim of the work is to study the effect of heavy metals (Pb, Zn, Cd) on the enzymatic activity of catalase and urease when vermicompost, sulfur-perlite-containing waste, and their mixture are introduced into the serozem soil.

#### Materials and research methods

To study the nature and degree of change in the activity of soil catalase and urease from the amount of lead, zinc and cadmium, experimental experiments were performed.

Vermicompost, sulfur perlite-containing waste, and mixtures thereof were introduced into gray earth soils contaminated with heavy metals, as well as uncontaminated (control).

Heavy metals are introduced in the form of readily soluble acetates in doses: 1) control (without making); 2) 0.5 MAC; 3) 2.5 MAC; 4) 5 maximum concentration limits. Calculation of metal concentrations was carried out on the basis of MAC values. The enzyme activity of urease was determined in soil samples. All analyzes were performed in triplicate. For the determination of metals, was used the voltammetric method using the TA-Lab instrument.

Catalase activity was determined by the method of A.Sh. Galstyan described by F.Kh. Khaziev [14]. Urease activity was determined by the method of Romeiko and S.M. Malinsky [11]. The method is based on the photometric measurement of the amount of ammonia (ammonium nitrogen) formed during the hydrolysis of urea under the action of urease by the formation of colored complexes with Nessler's reagent.

#### Research results and discussion

Catalase plays an important role in the processes of neutralizing hydrogen peroxide, toxic for soil living organisms, which enters the soil as a result of their high physiological activity during a period of favorable living conditions. The presence of heavy metals in the soil may affect the rate of decomposition of hydrogen peroxide by catalase [1].

As the results of our studies showed, when introduced into the gray earth soil, the intensive decomposition of hydrogen peroxide depends on the concentrations of lead, cadmium and zinc. With an increase in the content of the studied metals in the soil system, a decrease in

the activity of catalase is observed and, accordingly, the rate of decomposition of hydrogen peroxide is reduced.

As can be seen from table 1 of all studied ranges of concentrations of Pb, Zn, Cd, a decrease in catalase activity is observed. The greatest decrease in catalase activity was found for Cd, the smallest – for Zn.

Catalase activity when adding 5 MAC Cd decreases by 42% compared with the control, with 5 MAC Pb – by 38%, with 5 MAC Zn – by 29%. The results obtained, indicating a sharp decrease in the catalase content with an increase in the content of HM in the soil system, are explained by the toxic effect of HM on microorganisms, accompanying the death of a significant part of them. A decrease in the quantitative content of microorganisms that are sources of catalase enzyme production, respectively, leads to inhibition of the decomposition of hydrogen peroxide.

Thus, the enzymatic activity of urease, regardless of the presence of all the studied metals, increases when vermicompost and sulfur perlite-containing waste are introduced into the soil system, i.e., the presence of HM does not cause a significant change in the level of soil fertility.

The results of the experimental data obtained by studying the effects of the content of HM (Pb, Zn, Cd) and the presence of vermicompost (VK), sulfur perlite-containing waste (SPW) on the enzymatic activity of urease are presented in table 2.

Table 2 shows an increase in the enzymatic activity of soils with the addition of vermicompost, sulfur-perlite-containing waste and their mixture, which indicates an increase in soil fertility. Moreover, this is observed for all concentrations of HM (Pb, Zn, Cd) introduced into the soil system.

**Table 1**  
Change in the activity of catalase when fertilizer-ameliorants are added to serozem contaminated with heavy metals (Pb, Zn, Cd)

Heavy metals and their concentrations, MAC		Catalase activity (the amount of oxygen released, in terms of 1 g of soil)			
		Soil	Soil + VK	Soil + SPW	Soil + VK + SPW
Pb	0(control)	2,2	2,3	2,3	2,4
	0,5	2,1	2,1	2,2	2,3
	2,5	1,9	2,0	2,1	2,1
	5,0	1,8	1,8	1,9	2,0
Zn	0(control)	2,2	2,3	2,3	2,4
	0,5	2,1	2,2	2,2	2,3
	2,5	2,0	2,1	2,2	2,1
	5,0	2,0	2,0	2,1	2,0
Cd	0(control)	2,2	2,3	2,3	2,4
	0,5	2,0	2,0	2,1	2,1
	2,5	1,8	1,9	2,0	1,9
	5,0	1,7	1,8	1,8	1,7

Table 2

Change activity of urease when fertilizer-ameliorants are added to serozem contaminated with heavy metals (Pb, Zn, Cd)

Heavy metals and their concentrations, MAC		Catalase activity (the amount of oxygen released, in terms of 1 g of soil)			
		Soil	Soil + VK	Soil + SPW	Soil + VK + SPW
Pb	0(control)	16,203	16,413	17,615	16,477
	0,5	16,322	17,417	17,810	16,620
	2,5	16,567	17,887	17,953	16,833
	5,0	16,673	17,940	17,967	16,940
Zn	0(control)	16,203	16,413	17,615	16,477
	0,5	13,780	17,973	16,917	16,650
	2,5	14,401	17,792	17,773	16,397
	5,0	15,150	16,920	17,807	16,026
Cd	0(control)	16,203	16,413	17,615	16,477
	0,5	16,207	16,063	15,557	14,803
	2,5	15,983	15,883	15,209	14,730
	5,0	14,032	15,407	15,043	14,224

The presence of Zn and Cd inhibits the enzymatic activity of urease. With an increase in their content, a decrease in the activity of this enzyme is clearly manifested, which leads to an inhibition of the reaction rate of urea decomposition.

Thus, the enzymatic activity of urease, regardless of the presence of all the studied metals, increases when vermicompost and sulfur perlite-containing waste are introduced into the soil system, i.e., the presence of HM does not cause a significant change in the level of soil fertility.

### Conclusion

Based on experimental studies, a change in some indicators of the biological activity of the soil, i.e. catalase and urease activity from the content in the soil of heavy metals (lead, zinc, cadmium).

HM, depending on their nature, have a different effect on the activity of catalase and urease in the soil system. In the case of the presence of Pb in the soil, an increase in the concentration of urease is observed with increasing metal concentration, i.e. Pb is involved in the decomposition of urea and activates the soil. Catalase activity decreases with a high concentration of Pb. Because lead slows down the process of decomposition of hydrogen peroxide and this reduces the level of oxygen metabolism in the soil system. The presence of heavy metals such as zinc and cadmium decreases the enzymatic activity of catalase and urease, which indicates an inhibition of the formation of ammonia and carbon dioxide during the decomposition of urea, and the formation of oxygen from the destruction of the structure of hydrogen peroxide.

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