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MIGRATION OF HEAVY METALS IN THE SOIL PROFILE**Yakovets L.**

Candidate of Agricultural Sciences, senior lecturer of the Department of Botany, Genetics and Plant Protection, Faculty of Agronomy and Forestry, Vinnytsia National Agrarian University
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Abstract

The problem of pollution of the soil environment with heavy metals is analyzed. Of particular importance is the profile migration of pollutants, which occurs most intensively in spring, autumn and summer with a large amount of precipitation, when there are intense descending flows of soil moisture. The migration of heavy metals is limited by the processes of their deposition on geochemical barriers. The study of the profile migration and accumulation of heavy metals showed that metals have an unequal behavior in soils, a change in their content along the profile is noted.

The article examines the dynamics of the distribution of mobile forms of heavy metals in various soils of the Vinnitsa region, provides the results of determining the pH in these soils.

It has been established that trace elements in the form of inorganic salts are effective on acidic soils. In soils with a reaction close to neutral, their effectiveness decreases tenfold. In neutral and slightly alkaline soils, inorganic salts cannot contain trace elements in a water-soluble form, that is, in a form accessible to plants, and their effectiveness tends to zero.

Analyzing soil contamination with lead, cadmium, zinc and copper, it was found that their content was 8.1 times lower than the MPC, 5.38, 21.4 and 5.0 times, respectively. A high content of heavy metals in the soil was observed for zinc, compared with lead, cadmium and copper, it was 1.44, 8.23 and 1.78 times higher, respectively.

Keywords: migration; heavy metals; anthropogenic sources; capture ratio; fertilizer; trace elements.

Anthropogenic load causes a significant impact on agroecosystems. For modern conditions of the region, an urgent problem is to study not only the essence of the processes of optimization of soil regimes and soil cultivation, but also the issues of environmental monitoring and evolution of the soil cover, the study of ways to reduce anthropogenic pressure and its negative consequences [1].

The pollution of agroecosystems with heavy metals is an extremely important and urgent problem of our time. Their danger is determined by their ability to accumulate in the soil, to be included in the trophic chains and transmitted by them from plants to the human body.

Heavy metals are removed from the human body very slowly and are capable of accumulating mainly in the kidneys and liver, given that plant products, even from slightly contaminated areas, can cause a cumulative effect - a gradual increase in the content of heavy metals in the human body.

The term "heavy metals" is characterized by a wide group of pollutants, which has recently become widespread. In various scientific and applied works, the authors interpret the meaning of this concept in different ways. In this regard, the number of elements that belong to the group of heavy metals varies within wide limits. Numerous characteristics are used as membership criteria: atomic mass, density, toxicity, prevalence in the natural environment, degree of involvement in natural and man-made cycles. In some cases, the definition of heavy metals includes elements related to brittle (for example, bismuth) or metalloids (for example, arsenic). Most heavy metals such as zinc, lead, copper, and cadmium are toxic.

The negative consequences of anthropogenic impact on ecosystems have led to deep destruction of important components of the biosphere, disruption of its

functions, disintegration of almost closed natural biogeochemical cyclic processes in the biosphere and destruction of optimal conditions for the existence of living organisms, especially humans. Given the current circumstances, among the problems of modern ecology, one of the first places is occupied by agroecological aspects of soil use [2].

The main agroecological factors that directly affect the aggravation of the ecological situation in the region and a decrease in the stability of the environment, the destruction of the natural mechanisms of its stabilization (fauna and flora groups) include disruptions in the functioning of the carbon and nitrogen cycles, the intensification of various types of soil degradation, a decrease in their energy and buffer capacity [3].

To a large extent, the negative consequences of anthropogenic, quite often unreasonable, incompetent interference in natural ecosystems have manifested themselves today; scientific and public opinion is inclined to the need for the greening of all human economic activity.

The soil is a kind of natural workshop, where the processes of transferring vital chemical elements into a mobile state accessible to plants, or their consolidation and accumulation, are purposefully applied. The main processes, in which heavy metals are involved, are the processes of adsorption, migration, transformation, translocation by plants, removal into groundwater and inclusion in biogeochemical cycles. The localization of forms of heavy metals depends on a number of factors: the amount and composition of compounds inherited from the parent rock and coming from anthropogenic sources, interactions with soil components and soil solutions during secondary redistribution. The nature of these interactions is associated with the properties of

metal ions and with the composition and properties of soils. The forms of finding heavy metals in soils determine their mobility, migration ability, availability to living organisms and toxicity [1].

Soils function as a habitat, accumulator and sources of matter and energy for organisms, an intermediate chain between biological and geological circulation, a protective barrier and conditions for the normal functioning of the biosphere as a whole, and the like. The named functions of soils form their ecological potential.

The soil for heavy metals is a capacious acceptor. Once in the soil, metals firmly bind with humic substances, forming hardly soluble compounds, are part of absorbed bases, clay minerals, and also migrate in the soil solution along the profile.

The concentration of heavy metals in the soil solution is the most important ecological characteristic of the soil, since it determines the migration of heavy metals along the profile and their absorption by plants. Heavy metals contained in humic acids fixed on highly dispersed soil particles are a special migratory form of metals that plays an important role in the formation of mass flows that migrate in the solid runoff. The fixation of complex compounds of metals with humic acids on highly dispersed mineral components of the soil is a part of the global mechanism for regulating the mass transfer of metals in the biosphere.

Mobile forms of heavy metals are concentrated mainly in the upper soil horizons, where there is a lot of organic matter and biochemical processes are active. In organic complexes, heavy metals are highly mobile.

Heavy metals are fixed by organic matter in the following forms: salts with humic acids; as adsorbents of humic acids; in the form of complex salts with humic acids; as part of undecomposed and semi-decomposed plant and animal remains; in organometallic compounds, in the form of chelates, protenogenic amino acids, polyphenols.

In the presence of favorable soil conditions - high humus content and low acidity - heavy metals, with the exception of Cd, are well fixed by soil particles, passing into a stationary state.

The mobility of heavy metals also depends on the acidity of the soil. At pH 4, Pb and Hg are most mobile, pH values from 4.5 to 5 promote the mobility of Cu and Cr. Zn, Ni, Mn, and Co have the maximum mobility at pH from 5 to 5.5, and Cd is mobile at pH 6.5.

An increase in pH values enhances the sorption of cation-forming metals Cu, Zn, Ni, Hg, Pb and increases the mobility of anion-forming metals Mo, Cr, V. Strengthening of oxidizing conditions increases the migration ability of metals.

Thus, some part of technogenic heavy metals is in a mobile state in the soil solution, and a part goes into a stationary state, being fixed by organic matter, clay minerals and iron oxides.

Environmentally unjustified agricultural production led to significant losses of the humus layer of the soil, the development of erosion processes, an increase in the areas of acid and saline soils, a decrease in the

content of nutrients and beneficial microflora, contamination with pesticide residues, heavy metals, radionuclides.

Therefore, to solve the problems that have arisen in the field of land use, as well as to develop and implement scientifically based measures for the ecologically balanced use of agricultural land, it is necessary to have information on the agroecological state of soils.

The need to study the mobile forms of heavy metals is due to their high migration activity and the ability to accumulate in biological objects.

Most authors [2, 3] distinguish two groups of HM compounds in soils by the mechanism of interaction of metal with soil components and by methods of extracting HMs from the composition of soil components: weakly and strongly associated with soil components. A group is understood as a set of metal compounds that are similar in bond strength to soil components, and therefore have a similar migration ability and biological availability.

The group of loosely bound compounds includes HMs that are in an exchangeable and specifically sorbed state on the surface of soil particles. This group of compounds is the most important from an ecological point of view, since they enter plants and migrate to adjacent environments.

The group of tightly bound compounds: includes HMs that are firmly fixed in the structures of primary and secondary minerals of silicate and non-silicate nature, as well as in the composition of hardly soluble salts and stable organic and organomineral compounds.

The accumulation of the main part of pollutants is observed mainly in the humus-accumulative soil horizon, where they are bound by aluminosilicates, non-silicate minerals, and organic substances due to various interaction reactions. The composition and amount of elements retained in the soil depend on the content and composition of humus, acid-base and redox conditions, sorption capacity, and the intensity of biological absorption. Some of the heavy metals are firmly retained by these components and not only does not participate in migration along the soil profile, but also does not pose a danger to living organisms. The negative environmental consequences of soil pollution are associated with mobile metal compounds. [4]. Within the soil profile, the technogenic flow of substances meets a number of soil-geochemical barriers. These include carbonate, gypsum, illuvial horizons (illuvial-ferruginous-humus). Some of the highly toxic elements can transform into compounds that are difficult to reach for plants; other elements that are mobile in a given soil-geochemical environment can migrate in the soil layer, posing a potential hazard to biota. The mobility of elements largely depends on acid-base and redox conditions in soils. In neutral soils, compounds Zn, V, As, Se are mobile, which can be leached during seasonal soil wetting [5, 6].

The accumulation of mobile compounds of elements that are especially dangerous for organisms depends on the water and air regimes of soils: the least accumulation of them is observed in permeable soils of the permeable regime, it increases in soils with a non-flush regime and is maximum in soils with an effusion

regime. With an evaporative concentration and alkaline reaction, Se, As, V can accumulate in the soil in an easily accessible form, and under conditions of a reducing environment, Hg in the form of methylated compounds.

However, it should be borne in mind that under the conditions of a leaching regime, the potential mobility of metals is realized, and they can be taken out of the soil profile, being sources of secondary pollution of groundwater.

It is found that about 70% of lead is received by a person with food. The lead content depends on the region and averages 0.01-1 mg / kg of the product. Cadmium, accumulating in plants, easily gets into food products, and through them into the human body. Arsenic is present in most foods because it is widely distributed in the environment.

Heavy metals, getting into living organisms, accumulate in certain tissues, as a result of which a number of disorders occur at the cellular level. In particular, interacting with the thiol groups of various macromolecules of the body, they are blocked, which subsequently leads to the loss of many reactions by proteins and metabolic disorders. In the blood, heavy metals combine with albumin, which increases their availability to the cells of the body [4].

The ingestion of heavy metals into the human body for a long period negatively affects its hematopoietic organs, and also enhances the formation of free radicals, which leads to lipid oxidation. Heavy metal poisoning increases morbidity and shortens life expectancy, and there is a high stillbirth rate. The constant intake of heavy metals into the body leads to the emergence of a stress factor, as well as to latent changes in metabolism.

Cadmium poisoning leads to a decrease in immunity, increases the risk of diseases of the gonads and kidneys, is the cause of gastritis and anemia, spasm of arterioles and renal arteries. The consequence of poisoning is an increase in blood pressure, which leads to cardiovascular disease [5].

An excess of heavy metals in the body, in particular lead, cadmium and zinc, causes a number of disorders at all levels of the body, which leads to the emergence and intensification of various kinds of human diseases. In acidic soils with a predominance of oxidative conditions (podzolic soils, well-drained) such heavy metals like Cd and Hg, they form readily mobile forms. On the contrary, Pb, As, Se form inactive compounds capable of accumulating in humus and illuvial horizons and negatively affecting the state of soil biota. If S is present in the composition of pollutants, a secondary hydrogen sulfide environment is created under reducing conditions, and many metals form insoluble or poorly soluble sulfides [7].

In boggy soils, Mo, V, As, Se are present in secondary forms. A significant part of the elements in acidic boggy soils are present in forms that are relatively mobile and dangerous for living matter; such are the compounds Pb, Cr, Ni, Co, Cu, Zn, Cd and Hg. In weakly acidic and neutral soils with good aeration, poorly soluble Pb compounds are formed, especially during liming. In neutral soils, compounds Zn, V, As, Se are mobile, while Cd and Hg can be retained in the

humus and illuvial horizons. As the alkalinity increases, the risk of soil contamination by the listed elements increases [8].

Plants, like soils, are the most important link in the biological cycle of substances [9]. It should be noted that Zn, Cu, Pb are trace elements necessary for the normal life of plants. However, all metals in high concentrations are toxic to plants; therefore, it is more correct to speak not of toxic elements, but of toxic concentrations of elements for plants.

According to scientific researchers, metals can be arranged in the following toxicity series: Cu > Ni > Cd > Zn > Pb > Hg > Fe [9]. The trace element composition of plants depends on the content of exchangeable forms of these elements in the soil. Plants contain heavy metals in the form of cations. In the system, they can occur in the form of free ions (Zn²⁺, Cu²⁺, Pb²⁺) or as part of complexes with organic compounds.

The perennial organs (bark, roots) of plants absorb and accumulate heavy metals in the main barrier-free, that is, in direct proportion to the content of substances in the soil [10]. A high metal content is characteristic of leaves, generative organs and growth points. Desorption of heavy metals from solid soil sources and transport of soluble metals from the soil mass to the root surface determine their concentration in the rhizosphere. Heavy metals can be transported through the soil by exchange and diffusion.

There are two leading factors in the formation of the elemental composition of plants - genetic and ecological. Their equity participation varies depending on changes in environmental conditions. The ecological factor becomes the leading one in case of technogenic pollution of the habitat of heavy metals, especially their mobile forms. Pollutants enter plants both during root nutrition and by gas exchange and exchange adsorption from the surface of the leaf blade. After penetrating the root system, metal ions can remain there or move to the terrestrial parts of plants. An insignificant amount of trace elements can enter through the leaves from precipitation [10].

The coefficient of capture by plants of atmospheric aerosols of natural and technogenic origin ranges from 40–100%. In this case, toxic elements are characterized by the maximum absorption rates: Cd > Pb > Zn > Cu > Mn > Fe [10].

Plants have several control systems (or physiological barriers) for the intake of toxic elements, for example, absorption membranes, metal deposition in vacuoles, etc.:

- the first barrier to the entry of heavy metals from the soil into the terrestrial part of plants is the covering tissue of the roots, which has a significant selective adsorbing capacity.

- when metals penetrate into the cytoplasm of plant cells, chelate compounds are formed with almost 90% of heavy metals entering the cell, and thereby their participation in metabolism decreases.

- Tolerance to heavy metals in plants is genetically controlled and has a certain capacity, that is, under conditions of their excess in soils and in soil solutions, "forced" root absorption occurs, the ability of roots to retain metals is exhausted, they enter the leaves

and fruits. Therefore, at high pollution, the accumulation of heavy metals in plants is acropetal: roots> stems> leaves> fruits (seeds).

- different periods of plant ontogenesis differ in the degree of involvement of heavy metals in metabolism. The greatest accumulation is usually associated with the period of maximum activity or the period of preparation for rest [11].

One should take into account the fact that metals migrate in the form of ions and soluble metal complexes, their forms associated with dissolved organic or suspended inorganic and organic matter. The binding of metals by suspensions is carried out mainly by microplankton (bacteria, fungi, etc.) and dead remains of microorganisms, the specific surface of which is higher and contains more diverse active groups with high affinity for metals.

The accumulation of metals by microorganisms increases with an increase in their content in the environment. Metals accumulate in cells to a saturating concentration, after which, with a further increase in their content in the medium, the absorption of metals by cells does not increase. The accumulation of cells can last from several seconds to several hours [12].

Agricultural enterprises are the main sources of soil pollution.

At present, the application of fertilizers has been reduced to a minimum, but over a fairly long period of their use, the soils have accumulated a significant amount of heavy metals [13].

The content of heavy metals in fertilizers is shown in Table 1.

Table 1.

The elements	Fertilizers, mg/kg dry matter				
	Nitrogen	Phosphoric	Potash	Manure	Compost
Cu	1,0-15,0	10,0-17,0	186,4	28,8	Up to 1000,0
Zn	1,0-42,0	23,0	182,3	86,4	250,0
Pb	2,0-27,0	3,0-5,0	196,5	14,4	Up to 750,0

It has been established that trace elements in the form of inorganic salts are effective on acidic soils. In soils with a reaction close to neutral, their effectiveness decreases tenfold. In neutral and slightly alkaline soils, inorganic salts cannot contain trace elements in a water-soluble form, that is, in a form accessible to plants, and their effectiveness tends to zero. This is due to their transition into hardly soluble forms (hydroxides, carbonates) and a sharp cessation of their availability for assimilation by plants [14, 15].

For plants, the use of microelements is more effective in the form of metal chelates (chelates), they have a number of advantages. Thus, chelates are stable on all types of soils, regardless of their acidity level.

Manure is a significant source of cover for the removal of trace elements. But only at a rate of 13.5 tons of manure per 1 hectare of crop rotation area according to the organic-mineral fertilization system is almost compensated for their removal by crops, with the exception of manganese and boron.

Table 2.

Group number	Item content	mg per 1 kg soil			
		Boron	Manganese	Copper	Zinc
I	Very low	<0,15	<15	<0,70	<0,30
II	Low	0,15-0,22	15,0-20,0	0,70-1,00	0,30-0,50
III	Average	0,23-0,33	20,1-30,0	1,01-1,50	0,51-0,70
IV	Elevated	0,34-0,50	30,1-45,0	1,51-2,20	0,71-1,00
V	Tall	0,51-0,70	45,1-70,0	2,21-3,30	1,01-1,50
VI	Very tall	>0,7	>70	>3,30	> 1,50

According to soil studies on the content of mobile forms of microelements (Table 3), it can be concluded that the content of boron and manganese is within the

normal range. The sulfur content is low and the iron content is very low. Also, the magnesium content is increased.

Table 3.

The content of mobile forms of trace elements in the soil				
The mobile form of a trace element	Units	ND for research method	Soil security	Actual value
Mushroom boron	mg/kg	GOST 10 156-88	very high	2,86
Fly manganese	mg/kg	GSTU 4770.1-0017	very high	21,36
Fly sulfur	mg/kg	GSTU 8147-2015	low	5,3
Mushroom magnesium	mg-eq/100 g soil	GOST 26487-85	increased	2,42
Roll iron	mg/kg	GSTU 4770.1-0017	very low	1,56

Trace elements in the soil play an important role in plant nutrition. Since the content of iron and sulfur is low, as a recommendation, you can use sulfur and iron-

containing microfertilizers [16, 17]. The ecological state of the field is determined by the level of contamination with radionuclides (Cs137, Sr90), heavy metals

(cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn)), residues of DDT and HCH Implementation of such soil surveys will help farm specialists determine the need

for soil chemical reclamation, establish systematic work to improve soil fertility.

Table 4.

Intensity of soil pollution with heavy metals, mg/ g

Heavy metal	Actual content	MPC	CO
Lead	0,74	6,0	0,12
Cadmium	0,13	0,7	0,18
Zinc	1,07	23	0,04
Copper	0,60	3,0	0,2

Analyzing soil contamination with lead, cadmium, zinc and copper, we note that their content was 8.1 times lower than the MPC, 5.38, 21.4 and 5.0 times, respectively. A high content of heavy metals in the soil was observed for zinc, compared with lead, cadmium and copper, it was 1.44, 8.23 and 1.78 times higher, respectively.

So, the migration of heavy metals in the environment undoubtedly creates a potential danger for it, namely: pollution of soils, hydrosphere with heavy metals, etc. The nature and degree of soil stability in relation to pollutants is determined by the nature of the chemical bonds formed between pollutants in the soil solution and in the composition of equilibrium with them mobile compounds in the solid phase of the soil. Here, the simultaneous course of some chemical reactions is possible: precipitation - dissolution of pollutants in the form of hardly soluble precipitates (hydroxides, salts, complex compounds), exchange and non-exchange sorption-desorption on the active surface of solid soil phases. It has been proved that the pH of the medium has a tremendous effect on the migration of heavy metals in the soil, which is explained by the different solubility of their compounds depending on the pH of the soil solution - with an increase in pH, the concentration of mobile forms of metal in the soil solution decreases.

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