

## GEOCHEMICAL REGULARITIES OF HEAVY METALS DISTRIBUTION IN THE IRRIGATED ALLUVIAL SOILS OF THE MIDDLE DNIESTER MEADOW

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### ABSTRACT

The alluvial soils weakly or moderately evolved, irrigated from the middle Dniester meadow are characterized by stratified, loamy, weak or moderately humiferous profile, moderately carbonate. One of the significant characteristics of the distribution of heavy metals in the profile of these soils is the relatively high concentrations of most total and mobile forms in the depth horizons, due to their leached from the upper horizon, an additional supply of ground water, and a high content of organic matter. The fallow alluvial soils differ from the arable by a higher content of elements in profile, especially in the humus horizon, which is related to the specific conditions of their formation, geomorphological characteristics, hydrological regime, etc. Thus, in alluvial soils, approximately 50% of the total reserve of heavy metals are concentrated in the upper part of the profile. The distribution and accumulation of Zn, Co, Fe, Mn, Pb, Cu is associated with the biogenic accumulation in the soil layer of 0-23 cm. Accumulation at the geochemical barrier (57-80 cm) is evident - the beginning of the gleyic horizon. Maximum accumulations of Fe (47.7 mg kg<sup>-1</sup>), Mn (52.4 mg kg<sup>-1</sup>) and Zn (2.9 mg kg<sup>-1</sup>) are detected in the horizon (160-200 cm). Irrigated alluvial soils are not polluted with heavy metals: their concentration in the soil does not exceed the maximum permissible limits.

**Key words:** heavy metals, soil properties, river meadow, alluvial soil

### Introduction

In conditions of soil degradation and climate change, food security in the Republic of Moldova can be ensured by using alluvial soils near the Dniester River and expanding areas with irrigated soils in these areas. The most suitable areas for the development of irrigated agriculture are the lands in the river meadows with typical and strongly evolved alluvial soils. On the territory of the Republic of Moldova, within the lands with agricultural destination, the alluvial (meadow) soils occupy the surface of about 117 thousand ha (26). A major interest in expanding agriculture and irrigation is the evaluation of heavy metals in the alluvial soils of the Middle Dniester meadow.

In the middle course of the Dniester (from Nijnee to Dubasari) (8), there are six terraces, mostly under arable land, but also occupied by orchards, gardens, vineyards, field crops. In the middle course of the river the riverbed is more strongly meandered than in the upper one, the length of the meanders reaching 12-15 km, and the radius of the arches 2-10 km.

The external appearance and condition of the Medial Dniester ecosystems during the last decades have undergone cardinal changes. The instability of the hydrological regime was expressed by the redistribution of the annual flow of the river, the sudden fluctuations of the level and flow, contributed to the spread of aquatic plants in the riverbed. The long period of drought led to a

considerable decrease in water flow speed and in the river part of the Middle Dniester. This in turn favored negative changes in terrestrial and aquatic ecosystems, intensified the processes of degradation of soil resources, intensified the processes of erosion on slopes, changed the vegetal composition of pastures, etc. The modified thermal regime of the middle sector of the Dniester also disrupted the natural process of self-purification of the basin (5).

On the territory of the Dniester district, typical alluvial soils are quite widespread in river meadows, occupying 10.2% of the country's territory, over 55% of them are salinized. The high degree of agricultural use of land in the Dniester district has a significant impact on the environment quality, affecting the ecological balance of ecosystems, causing soil degradation and desertification processes (23).

The soils on the Dniester district, due to the predominantly fragmented relief, especially in the central part, are intensely subjected to geodynamic processes, but also to significant anthropogenic impact caused by excessive deforestation, destruction of forest belts and riparian protection areas, irregular or poorly managed hydrotechnical works, excessive and uncompensated exploitation of mineral and organic reserves, etc. Even in the lower course of the Dniester, where the relief is quite smooth and soil erosion is not so pronounced, the loss of fertility of arable land due to erosion is estimated at 43.4% (29).

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## Material and method

The typical arable alluvial soils from the Middle Dniester meadow (Jora de Mijloc village, Orhei district) were selected as objects. Soil profiles up to a depth of 200 cm were placed on the land selected for research, from which soil samples were collected on genetic horizons. Heavy metals were determined by the method of atomic absorption spectrophotometry.

The soil cover was formed, for the most part, on Quaternary sediments, represented by clays, clay-sandy soils and sandy-loamy soils (especially in the floodplain of the Dniester). There are two main types: floodplain soils and soils on the terraces of the Dniester, where chernozems with full profile predominate.

Alluvial (meadow) soils are representative in the soil cover of the area. Floodplain soils are new alluvial soil formations in the Dniester river basin. Alluvial processes include on the one hand the erosion of the riverbed, which causes the periodic "rejuvenation" of the riverbed and the adjacent sectors of the meadow, and on the other hand accumulations on the surface of the meadow of solid river runoff. In the Dniester meadow there is a periodic flooding of its meadow with water from the river; In such cases the soils and the whole layer of alluvial deposits are considerably moistened. The flood conditions a hydromorphic character of soil formation on the meadow territory. An important feature of meadow soils is their high biogenesis, conditioned by the acceleration of the circuit of substances and the process of soil formation.

Alluvial soils, as a result of different conditions of manifestation of solifaction, zonal climate, origin of river deposits, their texture and composition, depth and mineralization of groundwater, are characterized by a very large variation of physical, chemical and geochemical properties. Arable use and irrigation act differently on the quality status of alluvial soil varieties, geochemical composition, their production capacity. In order to assess the physico-chemical and geochemical quality (migration and accumulation of heavy metals) of alluvial soils, further research is needed for the correct use of these soils in sustainable agriculture. The research area is an area where two ecosystems intertwine: natural pasture and agricultural ecosystem, which is also called - ecoton (4, 10, 31).

## Results and discussions

The high contents of heavy metals in the soil present a direct risk of soil pollution and therefore affect the plants that absorb them, the animals that consume those plants and implicitly humans. If not

recognized and treated properly, heavy metal toxicity can lead to morbidity and mortality. The accumulation of heavy metals in agricultural soils is associated with the use in agriculture of mineral fertilizers, plant protection products, organic waste, etc. At the same time, heavy metals are also considered microelements, because they are used by plants in very small quantities. The microelements are Fe, Mn, Cu, Zn, Ba, Ti, Li, I, Br, Al, Ni, Mo, As, Pb, Va, Rb, and others (22, 30, 32). When a necessary chemical element is missing or insufficient in plant nutrition, physiological diseases appear, accompanied by the slowing down or stopping of the growth of the root, stem, leaves, or fruits (28).

*Manganese (Mn)* has a stimulating role in plant growth, flower formation, synthesis of vitamins and carbohydrates. In glycolysis as in other processes in which phosphorylation is present, an important role is played by the presence of manganese, Mn ions activate various enzymes (1, 9). Mn ions lead to a higher activity of peroxidase in wheat grains induced by additional nutrition with Mn, but also a more intense catalysis activity. Manganese is needed to reduce nitrates. Manganese promotes the multiplication of bacteria from nodules to legumes, as well as the accumulation of a larger amount of nitrogen, by activating the enzyme system that catalyzes the reaction between hydroxylamine and glutamine derivatives. Mn supplementation promotes vitamin C content in tomatoes and cucumbers (12, 13).

The total Mn content in the typical alluvial soils is within the limits of 383 and 901 mg kg<sup>-1</sup>. The values of the total Mn fall within the limits determined for the soils of the Republic of Moldova (150-2250 mg kg<sup>-1</sup>), the average content being 790 mg kg<sup>-1</sup>. The upper horizon of the alluvial soil contains 830 mg/kg of Mn, and the lower ones (carbonate) - 383-510 mg kg<sup>-1</sup> of total Mn.

The mobile Mn content in the upper soil horizon of the Republic of Moldova varies between 0.4-195 mg kg<sup>-1</sup>. The values of Mn content accessible in the studied alluvial soils are between relatively average limits (43.6-89.4 mg kg<sup>-1</sup>), with a distribution very close to that described by the normal distribution law. As a result, the upper part of the soils has higher contents of accessible Mn than the middle glazed part. The highest Mn content (89.4 mg kg<sup>-1</sup>) was found in the glazed layer 81-110 cm, which shows the existence of a glyceemic geochemical barrier. The mobile Mn content has three maximum accumulations in the studied soils: in the humic horizon of the profile (0-23 cm) - 74.6 mg kg<sup>-1</sup> in the gleyic horizon (81-110 cm) - 89.4 and

in the lithological horizons (160- 180 cm) - 66.8 mg kg<sup>-1</sup>. Therefore, the distribution of mobile Mn in the alluvial soil profile cannot be described as uniform (Fig.1).

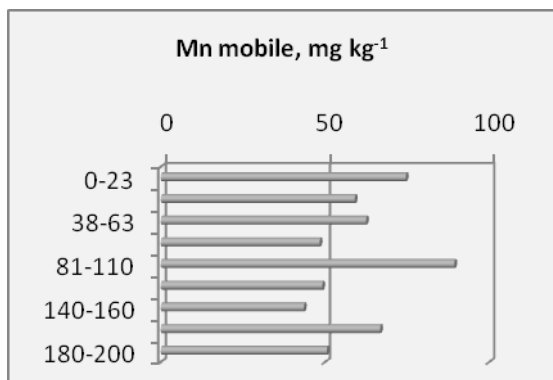


Fig. 1 - Mobile Mn content in typical alluvial soil

**Copper (Cu)** is part of the chemical composition of many substances used in agriculture. Copper is essential for all plants and has a role in chlorophyll formation, seed germination, increasing drought resistance and water supply. Controls respiration and protein synthesis. Cu is the component of phenoloxidase, lactase, ascorbic acid and oxidase. The copper content in plants varies from traces to 46 mg kg<sup>-1</sup>.

Lack of Cu from the plant is manifested by wilting of young leaves on potatoes, bleaching of leaves on salad. In cereals, the tips of the plants turn white, the leaves turn and die, the growth of internodes is stopped. At an intense deficiency the spike does not form. It is also reported especially in trees and cereals. Thus, in trees, young shoots have leaves with burnt or chlorinated edges (15, 16), and flowering and fruiting are stopped. Cu deficiency occurs mainly on swampy or post-swampy soils (meadow alluvial soils), which is manifested by wilting and discoloration to a white shade of young leaves. The total Cu content in the soils of the Republic of Moldova is estimated at the limits of 2 - 400 mg kg<sup>-1</sup>, with an average of 23 mg kg<sup>-1</sup>. In the studied soils The total Cu is in the range of 24-72 mg kg<sup>-1</sup>, which exceeds the average content for Moldovan soils.

The concentration of mobile Cu in soils varies in the range of 0.1-60.0 mg kg<sup>-1</sup>, with an average of 1.6 mg kg<sup>-1</sup>. The content values of Cu mobile in the researched soils oscillate between the limits (0.30-1.94 mg kg<sup>-1</sup>). Distribution of Cu mobile demonstrates higher concentrations in the humifer horizon (0-38 cm) - 1.74-1.94 mg kg<sup>-1</sup> and at the depth of the gleys horizon (38-81 cm). In the carbonate layer (110-180 cm) of the soil the content of mobile Cu is 0.30-0.45 mg kg<sup>-1</sup> (Fig.2).

**Zinc (Zn)** is indispensable for plants. It is absorbed by them from the living environment in the form of ions. It is widespread in lower plants (algae and fungi) and in higher plants. Zinc enters the chemical structure of enzymes: carbohydrase, phosphatase and many dehydrogenases.

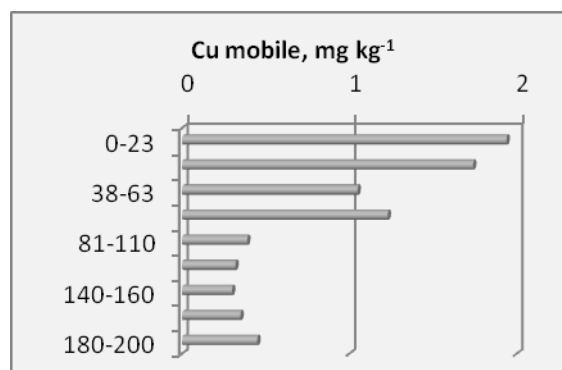


Fig. 2 - Mobile Cu content in typical alluvial soil

A good supply of Zn favors the increase of the content of tryptophan, a known precursor of auxin, and as a result the presence of auxin in the plant kg is favorably influenced (18). Zn increases the soluble sugar content, has an action on the viscosity of the protoplasm, due to the decrease in free water content (7). Zn has a role in chlorophyll synthesis, plant growth, increased resistance to drought and frost, in the fixation of nitrogen by legumes (14).

Zn deficiency in plants is manifested by the reduction of their growth, the arrangement in the rosette of the terminal branches and leaves, the yellow staining of the leaves, is manifested from the top of the plant to its base. In tobacco, vines, barley, sunflower appears the disease of "small leaves", in corn - bleaching of leaves. These plants are most sensitive to the lack of nutrition in zinc. Wheat, rye, oats and peas are less sensitive.

The maximum permissible limit for the total Zn content of the soil is 300 mg/kg (20). Anthropogenic sources of Zn are significant, coming mainly from industrial and agricultural activities, waste, etc. In the surface environment it has a moderately high mobility, limited by its tendency to be adsorbed on MnO<sub>2</sub> and by the insoluble organic matter in soils (32).

The total Zn content in Moldovan soils is estimated at the limits of 10-166 mg kg<sup>-1</sup>, with an average of 71 mg/kg. In alluvial soils the total Zn content is in the range of 38 and 77 mg kg<sup>-1</sup>. Accumulations of Zn are observed in the humic layers - 69 mg kg<sup>-1</sup> and in the carbonate layers - 72 mg kg<sup>-1</sup>, which does not exceed the average content for the soils of the Republic of Moldova. Lower

values of content are detected in the gleic horizons: 38-54 mg kg<sup>-1</sup> of Zn.

The mobile Zn contents determined in typical alluvial soils vary in wide limits (0.47-2.78 mg kg<sup>-1</sup>), with an important dominance of the contents in the deep layers (110-160 cm), in which 205-208 mg Zn/kg. These Zn concentrations are due to lithological genesis. In the soil profile the distribution is not uniform, it has two accumulations - in the humic and carbonate layer (Fig.3).

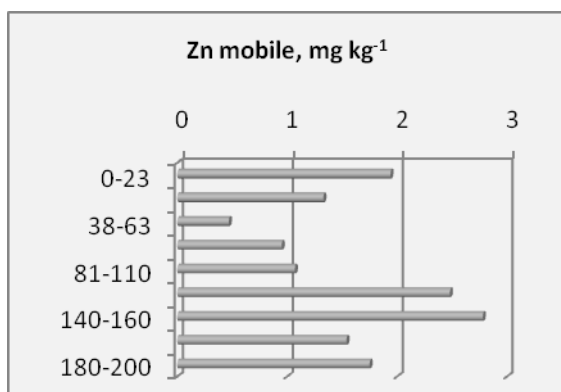


Fig. 3 - Mobile Zn content in typical alluvial soil

Zinc is an element with reduced mobility. The concentration of mobile forms Zn does not exceed the permissible limits for Moldovan soils - 4.9 mg kg<sup>-1</sup>.

**Cobalt (Co).** The maximum permitted limit for the total Co content of the soil is 50 mg kg<sup>-1</sup> (20). In soils, cobalt is found in various compounds in the form of ions (Co<sup>2+</sup>), present in the soil solution, adsorbed on the surface of colloidal particles, bound to organic matter, sesquioxides or present in the crystal structure of clay minerals or other minerals in the soil. Geochemical mobility in soils is mainly controlled by Co adsorption and co-precipitation with Mn and Fe oxides. Anthropogenic sources of Co in soils include: pesticides and fertilizers. Co-pollution environment problems are generally less significant than those associated with other heavy metals (2, 27).

The total Co content in Moldovan soils is on average 13 mg kg<sup>-1</sup>, and the limit values in the range of 4-18 mg kg<sup>-1</sup>. In the studied soils the total Co is in the limits of 8-13 mg kg<sup>-1</sup>. Higher amounts are detected in the second part of the profile: in the gleic layers: 13 mg kg<sup>-1</sup>.

The content of mobile Co in the upper horizon of alluvial soils is 0.64 mg kg<sup>-1</sup>, with a visible increase in depth - 0.89 mg kg<sup>-1</sup> in the soil layer 38-63 cm. Higher content was determined in the gleic layer (63-81 cm) - 1.59 mg kg<sup>-1</sup>, with a significant decrease in depth - 0.35-0.45 mg kg<sup>-1</sup>

(Fig.4). In the investigated soils, the Co content in the surface layer demonstrates a weak association with the organic matter in the arable layer 0-23 cm.

Accessible Co concentrations recorded in the studied soils oscillate in a fairly wide range, determined by the limits of 0.31 and 1.59 mg kg<sup>-1</sup>, which suggests a distribution belonging to the natural geochemical background.

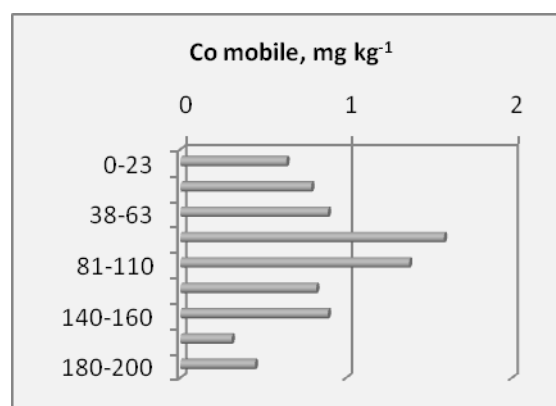


Fig. 4 - Mobile Co content in alluvial soil

**Lead (Pb)** has no known biological function, but is recognized as toxic to plant and animal life when present in ionic form. Because it behaves similarly to calcium, it is concentrated in the human and animal skeletal system. The total Pb content in Moldovan soils is in the range of 5-30 mg kg<sup>-1</sup>, with an average of mg kg<sup>-1</sup>. The values of the total Pb contents determined in the alluvial soils are within the average limits: 10-18 mg kg<sup>-1</sup>, which suggests a distribution between the normal limits for this element. Typical alluvial soils are characterized by a Pb content that decreases in the depth of the profile. Two accumulations are outlined in the profile of the studied soils: one in the upper part and the second, more pronounced in the lower part of the profile, at a depth of 160-180 cm.

The mobile forms of Pb in alluvial soils are estimated in the wide limits: 0.65-1.37 mg kg<sup>-1</sup>, which exceed the average for Moldovan soils are: 0.4 mg kg<sup>-1</sup>. Higher concentrations are detected at the top of the profile, with significant decreases in depth (Fig.5).

**Chromium (Cr)** is considered one of the most harmful heavy metals for human health (17). The uses of Cr are: in stainless steels, numerous alloys, Cr plating, pigments, catalysts, dyes, tannins, wood impregnation, refractory bricks, magnetic strips (27).

The total Cr contents in alluvial soils were estimated at 177 and 236 mg kg<sup>-1</sup>. The average values for Moldovan soils are equal to 91 mgCr/kg of soil, and the variation limits are 25-145 mg kg<sup>-1</sup>. Thus alluvial soils contain total Cr above the

allowed limits, emphasizing a significant accumulation - 1.9-2.6 times more than the limits.

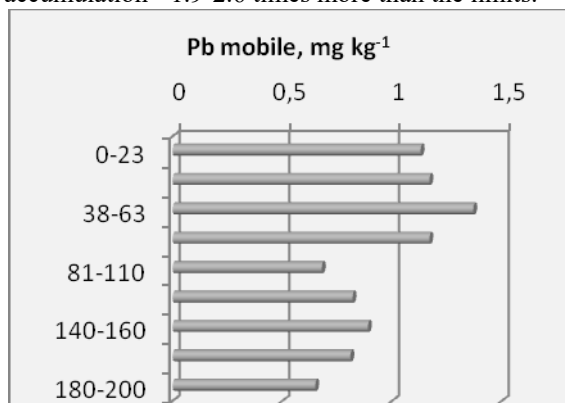


Fig. 5 - Mobile Pb content in typical alluvial soil

The content values determined for mobile Cr in the soils of the researched area range from 1.32-2.54 mg kg<sup>-1</sup>. The mobile Cr distribution in the researched soils appears to be very close to a natural one, with higher concentrations in the humifer horizon (0-23 cm) - up to 2.54 mg kg<sup>-1</sup>. In alluvial soils the biogenic accumulation takes place in the humic layers, with decreases in depths, proportional to the organic matter content (Fig. 6).

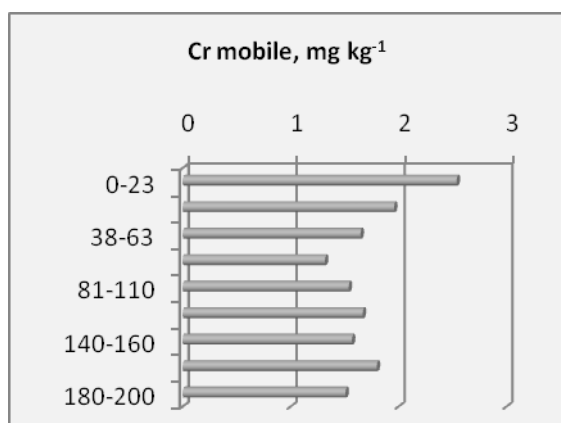


Fig. 6 - Mobile Cr content in typical alluvial soil

**Cadmium (Cd)** reaches the environment in three important ways: refining and using Cd, melting Cu and Ni ores and burning fossil fuels. The percentage level of Cd load in the sewage sludge is a problem in terms of its discharge and limiting or preventing the application of sludge on land as fertilizers. Increased use of Zn in fertilizers can lead to Cd contamination. Phosphate fertilizers contain between 5 and 100 mg kg<sup>-1</sup>Cd, and up to 300 mg kg<sup>-1</sup>Cd can be present in the sewage sludge.

This enrichment of Cd in the soil has several possible causes: anthropogenic pollution due to the chemical fertilizers used in agriculture; possible

upward movement in soils due to repeated re-precipitation; and association with organic matter, which is more abundant in the surface of the soil.

The maximum permitted limit for the total Cd content of the soil is 3 mg kg<sup>-1</sup> (20), equal to the value of the alert threshold for a sensitive use of the soil, and the value of the intervention threshold for the same type of use is 5 mg kg<sup>-1</sup>. Cadmium belongs to the same group (II) as Zn of the periodic table and as a result has many properties in common. In the soil surface, it has a good correlation with Zn, Mn, Pb and a poor correlation with Co and Cu (19). The average concentration of total Cd in Moldovan soils is 0.41 mg kg<sup>-1</sup>, and the permissible limits are 0.2-0.84 mg/kg. Higher Cd contents are detected in the upper part of the profile - up to a depth of 110 cm, constituting 1.09-1.26 mg kg<sup>-1</sup>. These values can be considered high for alluvial soils compared to the average content for Moldovan soils. Taking into account the pedogenesis of these soils, these values are admissible.

The content of mobile Cd is in the range of 0.01-0.3 mg kg<sup>-1</sup>, and the average is 0.04 mg/kg (6). Cd mobility in alluvial soils and their accumulation in the upper horizons is amplified by the low content of organic matter and their texture. In the upper part of the studied soil profile, the concentration of mobile Cd forms is higher (0.30 mg kg<sup>-1</sup>), than in depth (in the parent rock) - 0.18 mg kg<sup>-1</sup>. Cd accumulates at a depth of 81-140 cm (gleyic horizons) - 0.33 mg kg<sup>-1</sup> (Fig.7).

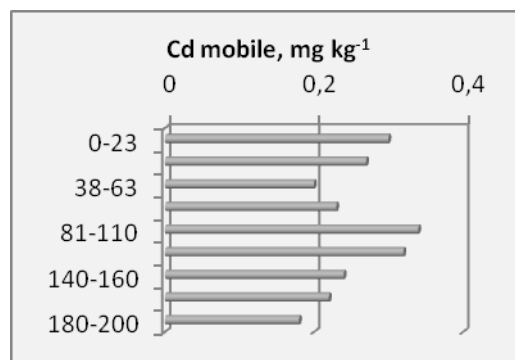


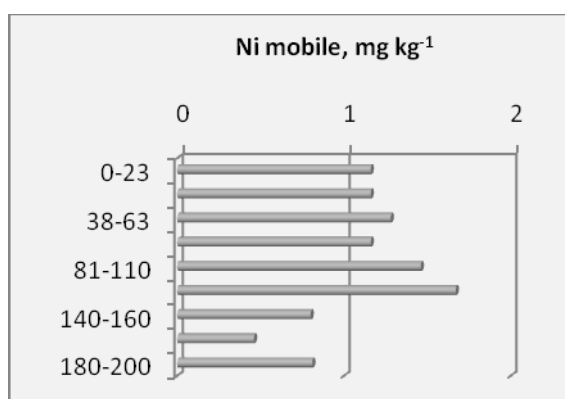
Fig. 7 - Mobile Cd content in typical alluvial soil

The studied alluvial arable soils are moderately evolved, therefore Cd accumulates depending on the organic matter and the texture of the layers, but the abundance of Cd predominates in the upper and middle part of the profiles.

**Nichel (Ni).** The maximum allowable limit for the total Ni content in the soil is 50 mg kg<sup>-1</sup> (20, 24). No biological role is known for Ni. Anthropogenic sources of Ni in agricultural soils include fertilizers (30). The total Ni contents in the

alluvial soil profile are between 10 and 12 mg kg<sup>-1</sup>, values that fall within the allowable limits (5-75 mg kg<sup>-1</sup>) for Moldovan soils. The average total Ni content in the country's soils is estimated at 39 mg kg<sup>-1</sup>. The total Ni content in alluvial soils is 4 times lower than the average content.

The mobile Ni contents determined in alluvial soils are between the limits: 0.46-1.67 mg/kg, values that exceed the limit of the normal ones (0.80 mg kg<sup>-1</sup>) for Ni in the humic and gleyic layers (Fig.8).



**Fig. 8** - Mobile Ni content in typical alluvial soil

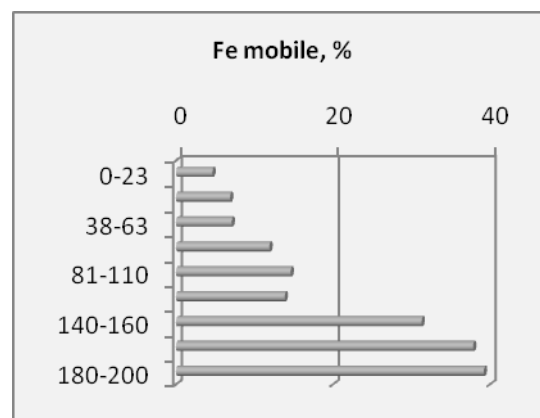
These concentrations suggest a natural distribution of Ni in the researched soils, disturbed only to a small extent by irrigation. From this it can be deduced that, on the thickness of the soil profiles, the Ni contents have an increased variation.

**Iron (Fe)** is found in the soil in the form of amphoteric oxides or hydroxides. In the soil surface horizons the most abundant are the hydrated happy oxides. In these horizons the total iron content oscillates, on average between 1.5 and 3.0% Fe in luvic soils, between 3.8 and 4.8% Fe in chernozems and between 5.7 and 12.5% Fe in soils of blond earth type. In soils rich in organic matter, iron is present in the soil solution as a bivalent ion or is retained by adsorption in the form of ferric hydroxide, insoluble and inaccessible to plants (40).

Iron is used by plants in the form of ferrous salts. It is absorbed by terrestrial plants through the root system, and by aquatic plants, submerged throughout their body in the form of ions. Iron is a microelement with a catalytic role and a dynamic role. It is present in large quantities in spinach, nettle and tea. Iron deficiency in plants causes the leaves to turn yellow and slow down their growth. In general, soils contain enough soluble iron necessary for plant nutrition. Insufficiency is caused by a number of factors, the most important of which are the alkaline reaction and the calcium carbonate content, most of

which is active. Iron is needed for the enzymatic synthesis of chlorophyll in plants.

Alluvial soils contain enough total iron: 2.34-3.40%. The legitimacies of distribution are manifested by the increase of the content in depth, the gleic horizons with higher content of total Fe are highlighted. In the investigated soils, the distribution of mobile Fe content varies between high limits: 4.65-39.23 mg/kg of Fe (Fig.9).



**Fig. 9** - Mobile Fe content in typical alluvial soil

This distribution is apparently a consequence of the variability of the pedogenesis of alluvial soils in the investigated area, as well as of the various land uses. The lower Fe content is, with few exceptions, characteristic of the upper layers of alluvial soils. Soils with an Fe content higher than 12 mg kg<sup>-1</sup>Fe are found in deep gleyic layers. The distribution of Fe in the investigated soils can be shown to be natural, only slightly affected by anthropogenic factors - arable use and irrigation. The content of Fe mobile forms in the deep of horizons varies between 31-39 mg kg<sup>-1</sup>. The distribution of Fe in alluvial soils indicates its accumulation at 160-180 cm. In general, alluvial soils contain enough soluble Fe for plant nutrition.

**The ecological situation in the researched area.** Several problems contribute to the degradation of natural resources in the area. First, there is a lack of an area management body that could protect biodiversity and provide sustainable development in the region. Natural forest and grassland ecosystems have a relatively small area and are isolated, being surrounded by extensive arable land and artificial plantations. Agriculture has greatly contributed to the degradation of steppe vegetation. The system of forest curtains along the waters is poorly preserved and protected.

Irregular grazing is practiced, mainly on meadows and edges. Likewise, it is sewn unsystematically, the floristic composition being

modified, and the grassy carpet of the meadows becoming degraded and weeded. The steppe lands occupy, mainly, steep slopes impassable for agriculture, which are affected by landslides and grazing. At present, no measures are being taken for the care and reconstruction of pastures.

In terms of actions to improve the ecological situation in the region, local land development plans are currently lacking, including landscape development plans, anti-erosion measures and soil condition monitoring. One reason is that the legislation does not provide for a control mechanism and an obligation to take appropriate action. Another cause is the almost total lack of proper crop rotation, which is based on perennial forage crops. Some private agricultural sectors are located right on the riparian water protection strip, which is forbidden (23, 26, 30).

Agriculture is a very important source of pollution that makes a significant contribution to soils and especially to areas where intensive agriculture is practiced. The main sources with potential polluting character in this area are: - impurities from fertilizers containing: Cd, Cr, Mo, Pb, U, V, Zn; - sewage sludges containing: Cd, Ni, Cu, Pb; Zn and many other elements; - organic residues from animal husbandry, in particular pigs and poultry, containing: Cu, As, Zn; - pesticides containing: Cu, As, Hg, Pb, Mn, Zn; - compost wastes (not necessarily used in agriculture) containing: Cd, Cu, Ni, Pb.

Most agricultural and horticultural soils are regularly fertilized with chemical and organic fertilizers. The concentration of heavy metals in these materials used as chemical fertilizers, organic fertilizers, amendments and composts in agricultural waste can be important sources of heavy metals. Chemical phosphorus fertilizers are an important source of Cd in soils and can have an acidifying effect and therefore facilitate the mobilization and advanced absorption of Cd in plants. Organic fertilizers contain many metals in differentiated assortment and high concentrations. Organic pig and poultry fertilizers have high Cu and Zn contents in addition to as which is used in feed (22).

However, the beneficial properties of sludge are limited by their content in potentially hazardous substances such as heavy metals and organic micro-pollutants (pesticides). Although all sludge contains a wide variety of metals and other contaminants in different concentrations, those in industry have the highest metal content. Heavy metals are most likely the cause of problems for agricultural products obtained on soils fertilized with sludge and which have high contents of Cd, Cu, Ni and Zn.

Due to the high concentration of heavy metals in used sludge, they are an important source of pollution when used. Due to the relatively small percentage of agricultural land on which used sludge is applied, it remains a less important source for many heavy metals (3, 11).

Heavy metals are toxic when they reach concentrations close to the maximum allowable limit. The control and quality of plant foods is a major problem for the health of the population, due to the negative implications of heavy metals in the metabolism of the human body. Tracking the pollution of agri-food products with heavy metals is a current problem, the respective chemical species are complexed with organic or inorganic ligands, which influences their toxicity.

The overall effect of heavy metal pollution is to reduce soil fertility and worsen plant nutrition conditions, influencing their growth and development processes. Inorganic toxins influence the growth and development processes of plants, the process of photosynthesis and the water absorption regime (15, 25). Pollution of soils with heavy metals had the effect of acidifying them and debasifying the absorbed complex. At the same time, the quality of organic matter is degraded by increasing the content of fulvic acids that form with heavy metals compounds with an advanced degree of mobility and accessibility for vegetation (27).

As a result of pollution, there are imbalances in the mineral nutrition of plants. These nutritional imbalances are due both to the general unfavorable nutritional conditions (acid reaction, low content of phosphorus, calcium and magnesium) and to the passive absorption of air and soil pollutants, which have a toxic effect on plant tissues. The result of these imbalances is the reduction of growth, premature drying of vegetation, disappearance of fruiting and thus decreased production.

Among the major metallic pollutants, Pb and Cd occupy the first place being non-essential elements of living organisms. Cu and Zn are essential elements of organisms, they become toxic only beyond certain limits. Due to the interaction of heavy metal ions with proteins, a strong inhibitory action is exerted on the enzyme systems. The initiated reactions take place at the level of the cell membrane and are followed by the penetration of toxic substances into the cells, with changes in its normal physiology (15). Therefore, in nature there are no plant-friendly or unfavorable elements, it all depends on the amount available to the plants, the same element can exert favorable effects (in optimal doses) or unfavorable effects (in insufficiency or excess).

## Conclusions

The main feature of the composition of heavy metals in the profile of arable alluvial soils is the relatively high content of total and mobile forms in the humiferous horizon (0-23cm), due to their biogenic accumulation. On the other hand, although a stratification of the profile of alluvial soils persists, in them there is a general pattern of distribution of heavy metals, reflected by a reduction of Mn, Cu, Pb, Ni and an increase of Zn, Co, Cr, Cd, Fe from top to bottom, with 3 accumulation maxima: biogenic, gleyic, carbonate.

Arable alluvial soils have a higher content of chemical elements in the profile, especially in the humus horizon, which is related to the specific conditions of their formation, geomorphological characteristics, hydrological regime, etc. Thus, in arable alluvial soils about 50% of the total reserve of total heavy metal forms are concentrated in the upper part of the profile.

In general, with regard to the biogenic accumulation capacity in the humus horizon of arable alluvial soils (0-23 cm), the mobile forms of microelements are located in a decreasing series: Mn > Cr > Zn > Cu > Ni > Pb > Co > Cd; total forms: Cr > Cu > Zn > Mn > Pb > Ni > Co > Cd.

The distribution and accumulation of Mn, Cu, Zn, Cr, Cd, Pb, is associated with the biogenic accumulation in the soil layer of 0-23 cm. The accumulation at the geochemical barrier (61 cm) is obvious - the beginning of the gleyic profile. In the buried humic horizon (81-110 cm) the total and mobile forms of Mn (900 mg/kg) and Fe (3%) accumulated. In the carbonate layers (140-200 cm) the maximum accumulations of Zn, Co, Cr, Ni and Fe (38 mg/kg) are detected.

Typical arable alluvial soils are not polluted with heavy metals: their concentration in the soil does not exceed the maximum limits allowed for the soils of the Republic of Moldova. Under proper management, alluvial soils can be productive for a wide range of dryland crops, but due to the dry climate without irrigation, yields are small and very small. Barley, alfalfa and sunflower, and to a lesser extent winter wheat, are the most suitable crops. Under irrigation conditions, alluvial soils are widely used in vegetable growing.

In natural ecosystems, alluvial soils have a relatively low percentage of vegetation cover, consisting mainly of meso-xerophilous meadows on high ridges, or mesophilic meadows and willows on wet ridges. These soils, however, are very suitable for poplar forests, but also for sown meadows. The results on heavy metal content can be used to develop measures and recommendations on

sustainable use, protection and quality improvement of alluvial soils in the Medial Dniester Meadow.

## Rezumat

Solurile aluviale slab sau moderat evaluate irigate și neirigate din lunca Nistrului Inferior se caracterizează cu profil stratificat, sunt lutoase, negleizate, slab sau moderat humifere, cu profil humifer puternic profund, moderat carbonatice. Una dintre caracteristicile semnificative ale distribuției microelementelor în profilul acestor soluri sunt concentrațiile relativ ridicate a majorității formelor totale și mobile de elemente în orizonturile de adâncime, datorită levigării lor din orizont superior al profilului, o alimentare suplimentară cu apă freatică, și un conținut ridicat de substanțe organice implicate în fixarea elementelor. Solurile aluviale înțelenite diferă de cele arabile printr-un conținut mai ridicat de elemente în profil, mai ales în orizontul de humus, care este legat de condițiile specifice ale formării lor, caracteristicile geomorfologie, regimul hidrologic etc. Astfel, în soluri aluviale înțelenite și arabile aproximativ 50% din rezerva totală a formelor mobile de microelemente sunt concentrate în partea superioară a profilului. Distribuția și acumularea de Zn, Co, Fe, Mn, Pb, Cu este asociată cu acumularea biogenică în stratul de sol de 0-20 cm. Acumularea la bariera geochimică (57-80 cm) este evidentă - începutul profilului gleyic. În orizontul humifer (80-95 cm) s-au acumulat formele mobile de Cd și Ni. În orizontul gleyic (160-200 cm) sunt detectate acumulările maxime de Fe (47,7 mg/kg), Mn (52,4 mg/kg) și Zn (2,9 mg/kg). Conținutul de materie organică, pH-ul, oxizii, carbonații și conținutul de argilă au influențat concentrația de metale grele în solurile aluviale la barierele geochimice. Solurile aluviale irigate nu sunt poluate cu metale grele: concentrația lor în sol nu depășește limitele maxime admise.

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