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ECOLOGICAL AND GEOCHEMICAL ASSESSMENT OF ALLUVIAL SOILS IN THE MEDIAL DNIESTER AREA

TAMARA LEAH¹

Abstract: *The alluvial soils are characterized by a very large variation in the physical, chemical and geochemical properties as a result of the different pedogenesis conditions, the zonal climate, the origin of the river deposits, their texture and composition, the depth and mineralization of the groundwater. The main characteristic of the heavy metal content in the arable alluvial soil profile is the relatively high content of the total and mobile forms in the humiferous horizon (0-23 cm) due to their biogenic accumulation. On the other hand, although a stratification of the alluvial soil profile persists, there is a general pattern of heavy metal distribution reflected by reduction of Mn, Cu, Pb, Ni, an increase Zn, Co, Cr, Cd and Fe content - from top to bottom of profile, with 3 accumulation maxima: biogenic, gleyic and carbonatic barriers. The typical arable alluvial soils are not polluted with heavy metals: their concentration in the soil does not exceed the maximum admissible limits for soils of Moldova.*

Keywords: *Alluvial soil, Biogeochemical barrier, Heavy metals, Lower Dniester.*

JEL Classification: *Q: Agricultural and Natural Resource Economics, Environmental and Ecological Economics; Q2: Renewable Resources and Conservation; Q24: Land.*

INTRODUCTION

The appearance and condition state of ecosystems in the Medial Dniester area during the last decades had underwent cardinal changes. The prolonged period of drought led to a considerable decrease in the speeds of the water stream and in the fluvial portion of the Dniester River. This in turn favored negative changes in terrestrial and aquatic ecosystems, intensified soil resource degradation processes, increased erosion processes on the slopes, changed the vegetation composition of pastures, etc. [3]. In conditions of soil cover degradation and climate change, the food security in the Republic of Moldova can be ensured by using the typical and highly evolved alluvial soils from the Dniester river meadow and by expanding the areas with irrigated soils in these areas. In the territory of the Republic of Moldova, in the lands of agricultural destination the meadow alluvial soils occupy the area of about 120 thousand ha [14,18,19]. Alluvial soils are the main object for development of irrigated agriculture, because they can be easily provided with irrigation water from rivers. In this case, a major interest for the extension of agriculture and irrigation is presented by the evaluation of the sources of heavy metal pollution of the alluvial soils of the Medial Dniester meadow. Physical degradation of soils, characterized by deterioration of unfavorable physical structure and properties, takes place under the influence of agricultural technique and mechanisms, but also as a result of irrigation with water that does not meet the requirements. Most of the times, the degradation of the amelioration systems, especially the drainage systems, in the river beds causes salinization. Soil degradation is one of the critical factors that cause the imbalance of functioning and fragmentation ecosystems [2,4,23].

The influence of chemical fertilizers and phytosanitary products used in agriculture on different ecosystems has diminished considerably, but water and wind erosion of the soil leads to eutrophication of the river. Illegal grazing on the river banks also contributes to the deterioration of the vegetal cover and to the degradation of the meadow soils properties. Drainage systems no longer have full management. The canals are muddy and the water pumping is no longer undertaken due to high electricity prices. The malfunctioning state of the drainage system led to a dangerous degradation of the old Dniester riverbed and to the spread of soil salinization on the drained lands. On the other hand, this fact leads to the abandonment of land, the restoration of marshes and meadows, the stimulation of the transition to a justified ecological grazing and grazing [1,10].

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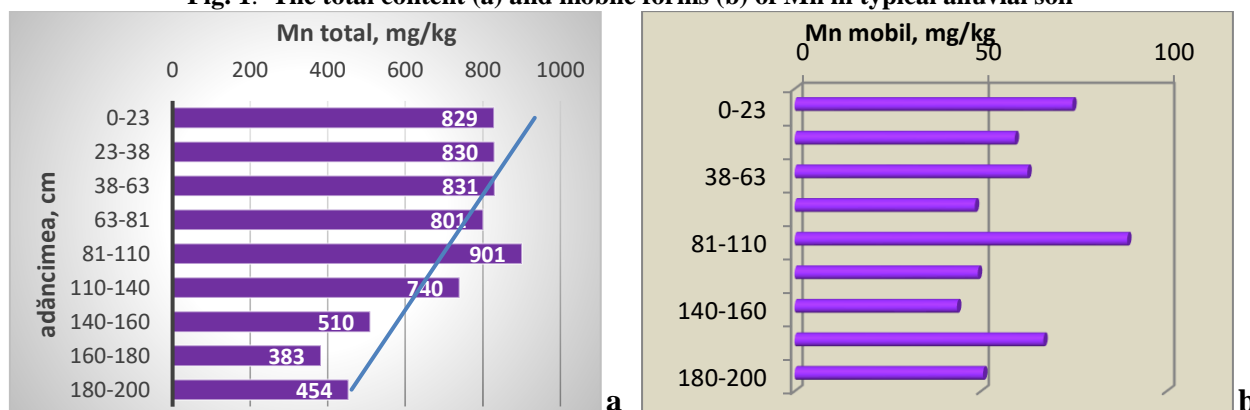
To assess ecological and geochemical assessment (migration and accumulation of heavy metals in the soil profile) of the alluvial soils, further research is needed for the correct use of these soils in sustainable agriculture. As an object, the arable typical alluvial soils from the middle Dniester meadow (Jora de Mijloc village, Orhei raion) were selected. Soil profiles up to 2 m depth were sampled on the field used for vegetables. The soil samples were collected on genetic horizons. The heavy metals were determined by atomic absorption spectrophotometry methods.

RESULTS AND DISCUSSIONS

Heavy metal pollution of meadow ecosystems occurs due to the lack of information on their impact on the environment and implicitly on the human body. Because of the conviction that the pollutants will be transformed or absorbed and thus the impact will be limited or non-existent [5,6]. The accumulation of heavy metals in agricultural soils is associated with the use in agriculture of fertilizers, plant protection products, organic waste, etc. Heavy metals are also considered microelements, as they are used by plants in very small quantities.

Manganese (Mn) is associated with Mg and Fe in silicate minerals. The distribution of MnO in soil is closely related to that of Fe₂O₃. The critical content of Mn is considered at 17 mg·kg⁻¹ (ppm). The excess of manganese produces toxic effects and manifests as brown spots, which appear on the older leaves [6]. The total Mn content in the alluvial soils is within the limits of 383 and 901 mg·kg⁻¹. The values of the total Mn content fall within the limits determined for the soils of the Republic of Moldova (150-2250 mg·kg⁻¹), the average content being 790 mg·kg⁻¹. The upper horizon of the alluvial soil contains 830 mg·kg⁻¹ of Mn, and the lower ones (carbonate horizon) - 383-510 mg·kg⁻¹ of total Mn (Fig. 1a).

Fig. 1. The total content (a) and mobile forms (b) of Mn in typical alluvial soil

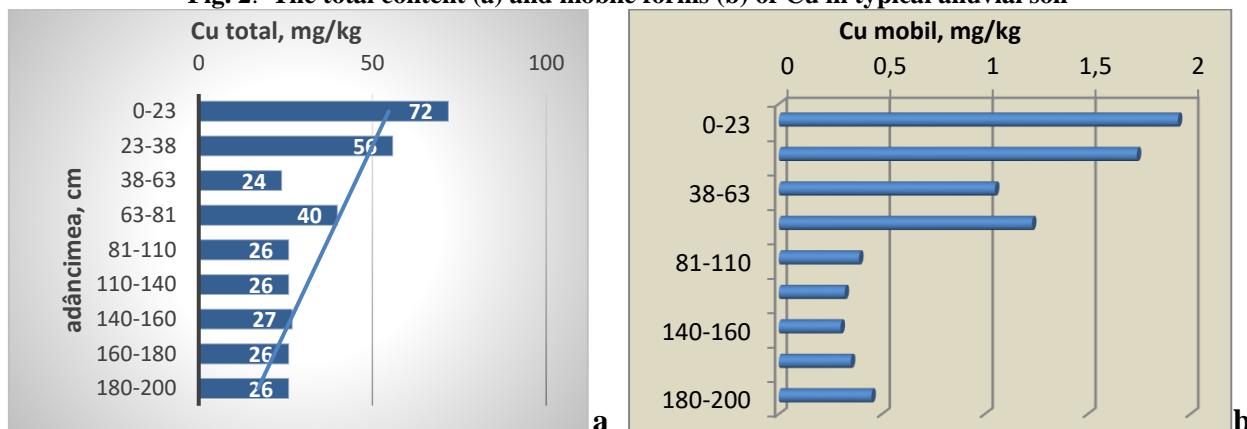


The content of mobile Mn in the upper horizon of the Republic of Moldova's soils varies between 0.4-195 mg·kg⁻¹ [8]. The content values of the accessible Mn in the studied alluvial soils are between relatively medium limits (43.6-89.4 mg·kg⁻¹), with a very close distribution that described by the normal distribution law. As a result, the upper part of the soils has higher contents of accessible Mn, than the middle gleyic part. The highest content of Mn (89.4 mg·kg⁻¹) was detected in the 81-110 cm of gleyic layer, which shows the existence of a geochemical gleyic barrier. In general, the content of mobile Mn has three maximum of accumulations in the studied soils: in the humiferous horizon of the profile (0-23 cm) - 74.6 mg·kg⁻¹, in the gleyic horizon (81-110 cm) - 89.4 and in the lithological horizons (160 -180 cm) - 66.8 mg·kg⁻¹. Therefore, the distribution of Mn in the alluvial soil profile cannot be described as uniform (Fig. 1b).

Copper (Cu) is association with other heavy metals: Pb, Zn, Mo, Ag, Ni etc. The geochemical mobility of Cu is intermediate, being controlled by the adsorption on oxides of Fe and Mn, by the presence of organic matter. Copper enters in the chemical composition of many substances used in agriculture. The maximum permissible limit for total Cu content in the soil is 100 mg·kg⁻¹

[9,11]. The total Cu content in the Moldovan soils is estimated at 2 - 400 mg·kg⁻¹, with an average of 23 mg·kg⁻¹. In the studied soils The total Cu is within the limits of 24-72 mg·kg⁻¹, which exceeds the average content for soils of Moldova. The highest quantity is associated with the organic matter, in the humiferous horizon (0-38 cm) it contains is 56-72 mg·kg⁻¹ of total Cu. Starting with a depth of 38 cm the total Cu content is decreasing (24-27 mg·kg⁻¹). A higher amount of total Cu is detected at the beginning of the gleyic horizon - 40 mg·kg⁻¹ (Fig. 2a).

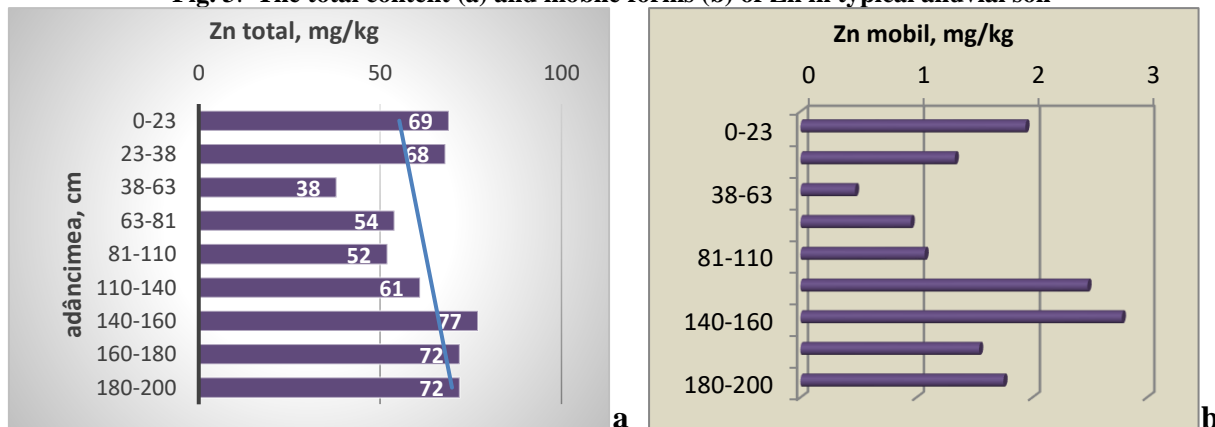
Fig. 2. The total content (a) and mobile forms (b) of Cu in typical alluvial soil



The concentration of Cu mobile in Moldovan soils varies within the limits of 0.1-60.0 mg·kg⁻¹, with an average of 1.6 mg·kg⁻¹. The content values of mobile Cu in the investigated soils range between the limits (0.30-1.94 mg·kg⁻¹). The distribution of mobile Cu demonstrates high concentrations in the humiferous horizon (0-38 cm) - 1.74-1.94 mg·kg⁻¹ and in the depth of the gegleyed horizon (63-81 cm). In the carbonatic layer (110-180 cm) of the soil the content of Cu mobile constitutes 0.30-0.45 mg·kg⁻¹ (Fig.2b).

Zinc (Zn) is present in soils, water, air and plants. At the topsoil part, Zn has a good correlation with Cd, Cu, Co, Mn, Fe, etc. The maximum permissible limit for the total Zn content in the soil is 300 mg mg·kg⁻¹ [9]. In the superficial environment it has a moderately high mobility, limited by its tendency to be adsorbed on MnO₂ and by the insoluble organic matter of soils [20]. The total Zn content in Moldovan soils is estimated at 10-166 mg·kg⁻¹, with an average of 71 mg·kg⁻¹. In alluvial soils the total Zn content is within the limits of 38 - 77 mg·kg⁻¹. Zinc accumulations are observed in humiferous layers - 69 mg·kg⁻¹ and in carbonate layers - 72 mg·kg⁻¹, which does not exceed the average content for the soils of the Republic of Moldova. In the yellow horizons, lower content values are detected: 38-54 mg·kg⁻¹ of Zn (Fig. 3a).

Fig. 3. The total content (a) and mobile forms (b) of Zn in typical alluvial soil

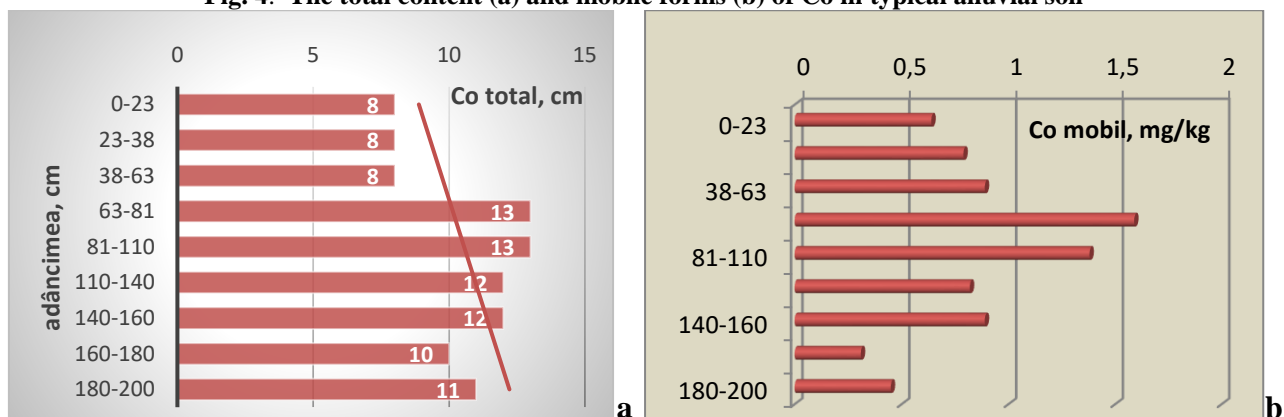


The mobile Zn determined in typical alluvial soils vary widely (0.47-2.78 mg·kg⁻¹), with a significant dominance of the contents in the deep layers (110-160 cm), containing 2.4 -2.8 mg Zn.

These Zn concentrations are the result of lithological genesis (Fig.3b). In the soil profile the distribution is not uniform, it has two accumulations - in the humiferous and carbonatic layers. Zinc is an element with reduced mobility. The concentration of mobile forms Zn does not exceed the permissible limits for Moldovan soils ($4.9 \text{ mg}\cdot\text{kg}^{-1}$).

Cobalt (Co) is present, in small quantities (traces), in rocks, soils, waters, plants and animals in the form of Co^{2+} ion. In the topsoil part, it has a strong correlation with Ni, Cr, Fe, Cu, and Mn [22]. The maximum permissible limit for total Co content in the soil is $50 \text{ mg}\cdot\text{kg}^{-1}$ [9]. Geochemical mobility in soils is mainly controlled by adsorption and co-precipitation of Co with Mn and Fe oxides [7]. The total Co content in Moldovan soils is on average $13 \text{ mg}\cdot\text{kg}^{-1}$, and the limit values in the range $4\text{-}18 \text{ mg}\cdot\text{kg}^{-1}$ [8]. In the studied soils the total Co is within the limits of $8\text{-}13 \text{ mg}\cdot\text{kg}^{-1}$. Higher quantities can be found at the bottom of the profile: in the gleyed layers - $13 \text{ mg}\cdot\text{kg}^{-1}$ (Fig.4a).

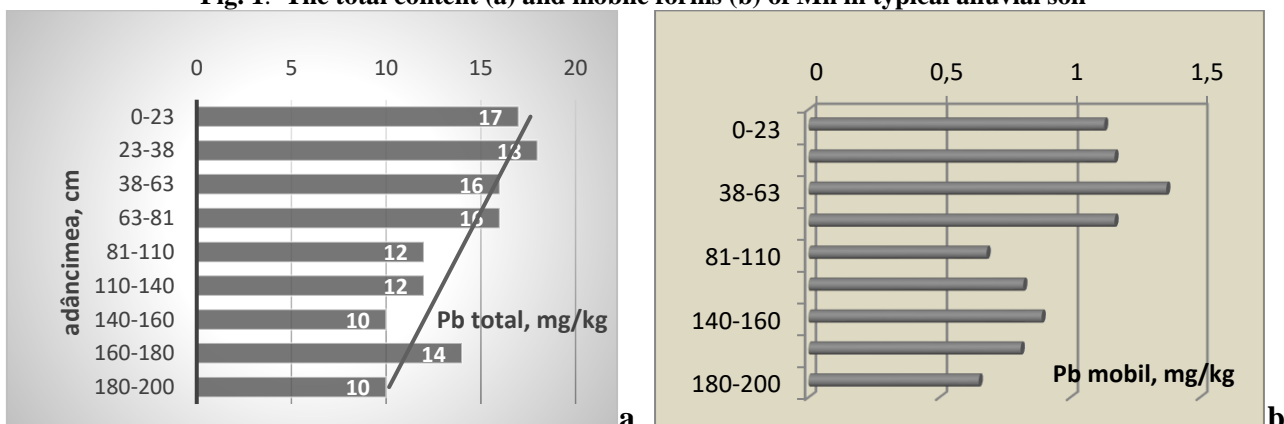
Fig. 4. The total content (a) and mobile forms (b) of Co in typical alluvial soil



The content of mobile Co in the upper horizon of the alluvial soils is $0.64 \text{ mg}\cdot\text{kg}^{-1}$, with a visible increase in depth, up to $0.89 \text{ mg}\cdot\text{kg}^{-1}$ in the soil layer of 38-63 cm. Higher content was determined in the gleuic layer (63-81 cm) - $1.59 \text{ mg}\cdot\text{kg}^{-1}$, with a significant decrease in depth - $0.35\text{-}0.45 \text{ mg}\cdot\text{kg}^{-1}$. In the investigated soils, the Co content in the topsoil layer shows a weak association with the organic matter in the arable layer 0-23 cm. The concentrations of accessible Co recorded in the studied soils oscillate in a rather wide range, determined by the limits 0.31 and $1.59 \text{ mg}\cdot\text{kg}^{-1}$, which suggests a distribution belonging to the natural geochemical background (Fig.4b).

Lead (Pb) content in the various types of soil around the globe, in a quasi-natural regime, is usually between $5\text{-}280 \text{ mg}\cdot\text{kg}^{-1}$, with an average value of $30 \text{ mg}\cdot\text{kg}^{-1}$ [12]. The maximum permissible limit for the total Pb content in the soil is $100 \text{ mg}\cdot\text{kg}^{-1}$ [9]. Lead has no known biological function, but is recognized to be toxic to plant and animal life, when present in ionic form [6,7]. The total Pb content in soils is in the range of $5\text{-}30 \text{ mg}\cdot\text{kg}^{-1}$, average - $20 \text{ mg}\cdot\text{kg}^{-1}$.

Fig. 1. The total content (a) and mobile forms (b) of Mn in typical alluvial soil

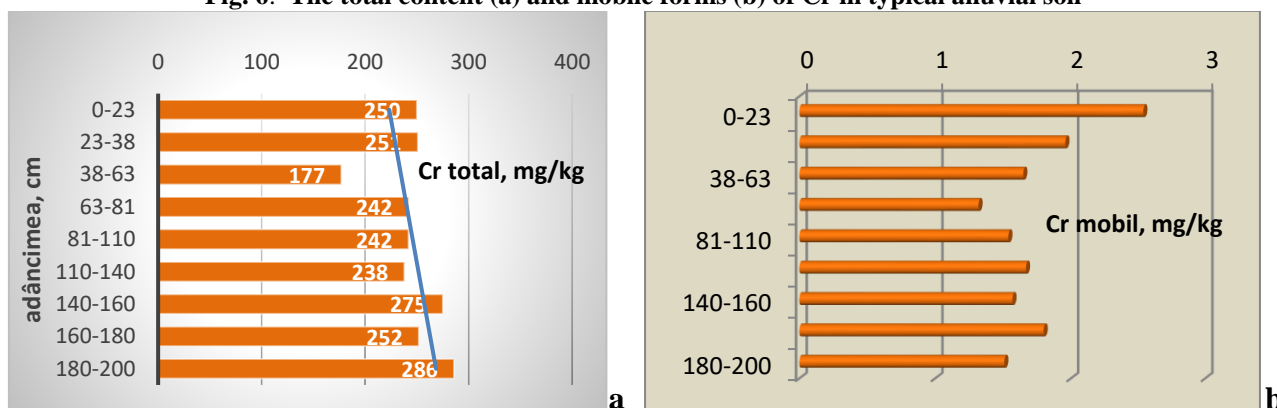


The values of total Pb content determined in alluvial soils fall within the average limits: 10-18 mg·kg⁻¹, which suggests a distribution between the normal limits for this element. Typical alluvial soils are characterized by Pb content that decreases in the depth of the profile. In the profile of the studied soils, two accumulations are outlined: one at the top and the second, more pronounced at the bottom of the profile, at a depth of 160-180 cm (Fig.5a).

The mobile forms of Pb in the alluvial soils are estimated within the wide limits: 0.65-1.37 mg·kg⁻¹, which exceed the average for the Moldovan soils: 0.4 mg·kg⁻¹. Higher concentrations are detected in the upper part of the profile, with significant decreases in depth, which is characteristic for alluvial meadow soils (Fig.5b).

Chromium (Cr) in the upper horizon of the various types of soil in the world, is usually between 1.4 and 500 mg·kg⁻¹, with an average value of 63 mg·kg⁻¹. The maximum permissible limit for total Cr content in soil is 100 mg·kg⁻¹ [9, 12]. The total Cr content in alluvial soils was estimated at 177 and 236 mg·kg⁻¹. The average values of Moldovan soils are 91 mg Cr/kg, the limits of variation constitute 25-145 mg·kg⁻¹. Thus the alluvial soils contain total Cr above the permissible limits, accentuating a significant accumulation - 1.9-2.6 times more than the limits. These concentration is characteristic for meadow soils (Fig.6a).

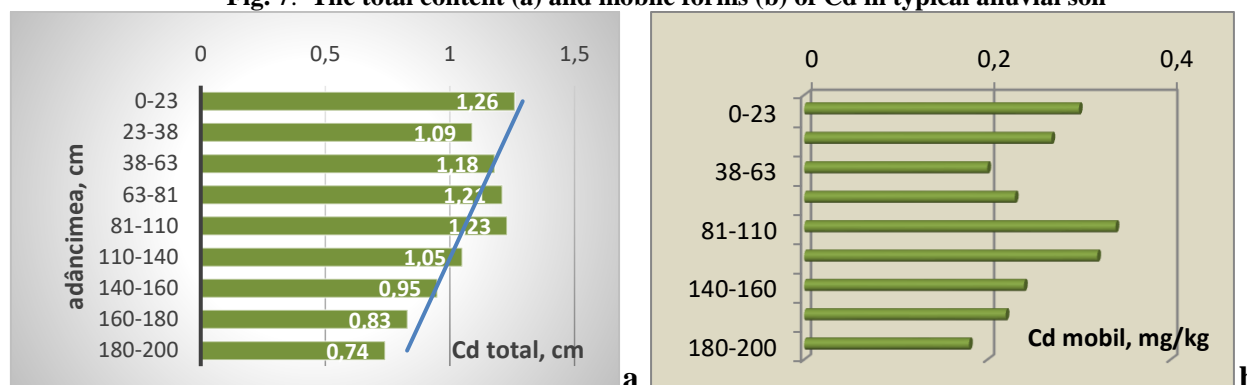
Fig. 6. The total content (a) and mobile forms (b) of Cr in typical alluvial soil



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

Cadmium (Cd) has a good correlation with Zn, Mn, Pb and a weak correlation with Co and Cu [7,21]. The Cd content in the upper horizon of the various types of soil worldwide, in natural quasi-regime, is between 0.01 and 2.70 mg·kg⁻¹, with an average value of 0.48 mg·kg⁻¹ [8,9]. The maximum permissible limit for total Cd content in the soil is 3 mg·kg⁻¹ [8]. The average concentration of total Cd in Moldovan soils is 0.41 mg·kg⁻¹ and the admissible limits 0.2-0.84 mg·kg⁻¹ [8]. Higher contents of Cd are detected in the upper part of the alluvial soil profile - up to a depth of 110 cm, constituting 1.09-1.26 mg·kg⁻¹. 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 in alluvial soils (Fig.7a).

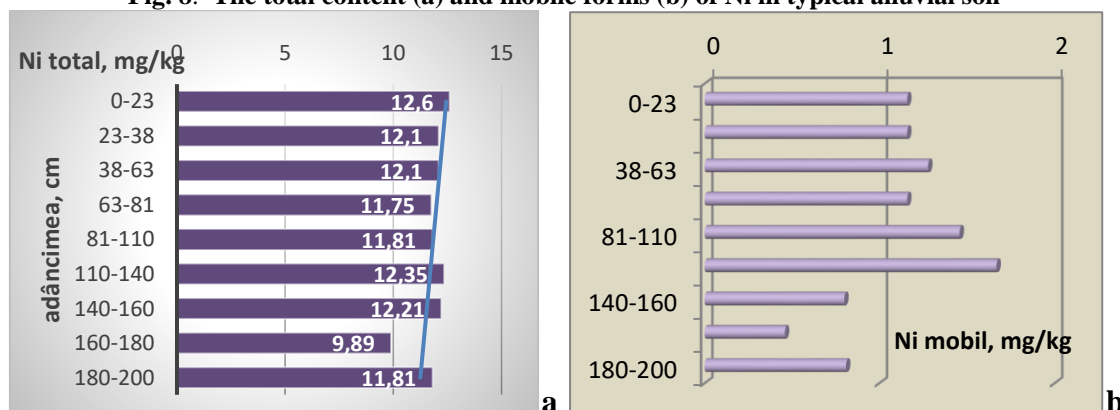
Fig. 7. The total content (a) and mobile forms (b) of Cd in typical alluvial soil



The mobile Cd content is within the limits of 0.01-0.3 mg·kg⁻¹ and the average constitutes 0.04 mg·kg⁻¹ [8,13]. 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 the mobile forms of Cd is higher (0.30 mg·kg⁻¹), than in the depth (in the parent rock) - 0.18 mg·kg⁻¹. Cadmium accumulates at a depth of 81-140 cm (gleyic horizon) - 0.33 mg·kg⁻¹ (Fig.7b). The arable alluvial soils studied are moderately evolved, which is why the Cd accumulates in dependence of the organic matter and the layers texture, but the abundance of Cd in the upper and middle part of the profiles predominates.

Nickel (Ni) enters into insoluble Fe oxides, which results in its relatively reduced mobility in the superficial environment. In ordinary waters it is present in very small quantities where it can withstand hydrolysis at pH > 6.5 [12,15,16]. The maximum permissible limit for total Ni content in the soil is 50 mg·kg⁻¹ [9,17]. No biological role is known for Ni. Anthropogenic sources of Ni include: use of fertilizers, detergents, etc. [21]. The total Ni contents in the alluvial soil profile are in average 11 mg·kg⁻¹, values that fall within the allowable limits (5-75 mg·kg⁻¹) for the soils of Moldova. The average content of total Ni in RM soils is estimated at 39 mg·kg⁻¹. The total Ni content in the alluvial soils is 4 times lower than the average content (Fig.8a).

Fig. 8. The total content (a) and mobile forms (b) of Ni in typical alluvial soil



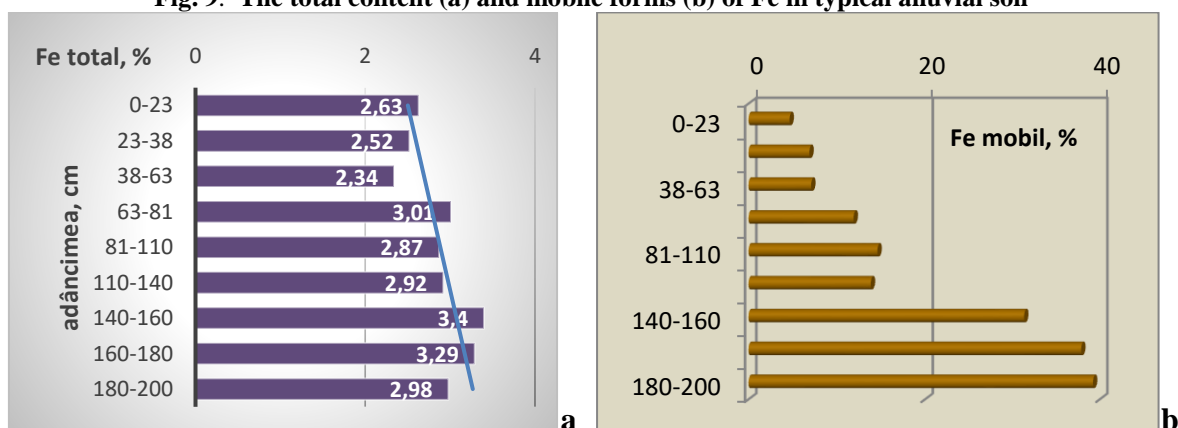
The contents of mobile Ni determined in the alluvial soils are between the limits: 0.46-1.67 mg·kg⁻¹, values that exceed the limit of the normal ones (0.80 mg·kg⁻¹) for Ni in the humic and gleyic layers. These concentrations suggest a natural distribution of Ni in the investigated soils, disturbed only 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 (Fig. 8b).

Iron (Fe). The estimated crustal abundance for Fe is 6.71%. On the superior part of the soil, there is a strong correlation with Co, Mn, Cu, Zn, a good correlation with Ni, and a negative correlation with SiO₂ (-0.50), statistically verifying the inverse geochemical relationship between Fe₂O₃ and SiO₂ [17,21]. The iron is found in the soil as amphoteric oxides or hydroxides.

In the surface horizons the most abundant are hydrated ferric oxides. In these horizons, the total iron content ranges from 1.5 to 3.0% Fe on average. In soils rich in organic matter, iron is present in soil solution as a bivalent ion or is retained by adsorption as ferric hydroxide, insoluble and inaccessible to plants [21,23,38]. In general, soils contain sufficient soluble iron necessary for plant nutrition. Insufficiency is caused by a number of factors, of which the most important are the alkaline reaction and the calcium carbonate content, most of which are active. Alluvial soils contain sufficient total iron: 2.34-3.40%. The distribution laws are manifested by the increase of the content in depth, the gleyic horizons with higher content of total Fe are highlighted (Fig.9a).

In the investigated soils, the distribution of mobile Fe content varies between high limits: 4.65-39.23 mg·kg⁻¹ of Fe (Fig.9b). This distribution is apparently a consequence of the variability of the pedogenesis of the alluvial soils in the investigated area, as well as of the various uses of the soil. The low Fe content is, with little exception, characteristic for the upper layers of alluvial soils. Soils with a Fe content more than 12 mg·kg⁻¹ are found in the deep-gleyic layers. The distribution of Fe in the studied alluvial soils can be proved to be natural, only slightly affected by anthropogenic factors - use in arable land and irrigation. The content of mobile forms of Fe in the depth horizons ranges from 31 to 39 mg·kg⁻¹. The distribution of Fe in the alluvial soils indicates its accumulation at a depth of 160-180 cm, this is sufficient soluble iron for plant nutrition.

Fig. 9. The total content (a) and mobile forms (b) of Fe in typical alluvial soil



The ecological situation. The main problems that contribute to the degradation of the natural resources in the researched area refer to: 1) - the lack of an area administration body, which could protect agricultural ecosystems and provide sustainable development in the region. The natural forest and grassland ecosystems have a relatively small surface area and are isolated, being surrounded by extensive arable land and artificial plantations. Agricultural practice has largely contributed to the degradation of the steppe vegetation. The system of forest curtains along the waters is poorly preserved and protected; 2) - the lack of local territory development plans, including landscape development plans, anti-erosion measures and soil status monitoring, for improving the ecological situation; 3) - total lack of a correct crop rotation, based on perennial forage crops; some private agricultural sectors are located right on the waterfront.

The main sources of potential pollutant character in this area are: - impurities from fertilizers containing: Cd, Cr, Mo, Pb, V, Zn; - sludge from wastewater containing: Cd, Ni, Cu, Pb; Zn and many other elements; - organic residues from livestock (pigs and birds), containing: Cu, As, Zn; - pesticides containing: Cu, As, Hg, Pb, Mn, Zn; - composted wastes (not necessarily used in agriculture) containing: Cd, Cu, Ni, Pb. Most of the agricultural and horticultural soils in this area 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 from waste in agriculture can be important sources of heavy metals.

CONCLUSIONS

The main characteristic of heavy metals in the profile of arable alluvial soils is the content of the total and mobile forms (Mn, Cu, Zn, Cd and Pb) relatively high in the humiferous horizon (0-23 cm) due to their biogenic accumulation. In arable alluvial soils approximately 50% of the total reserve of heavy metal are concentrated in the upper part of the profile. Accumulation at the geochemical barrier (61 cm) is evident - the beginning of the gleyic profile. In the buried humiferous horizon (81-110 cm) the total and mobile forms of Mn (900 mg·kg⁻¹) and Fe (3%) were accumulated. The maximum accumulations of Zn, Co, Cr, Ni and Fe are detected in the carbonate layers (140-200 cm). One of the significant characteristics of the distribution of heavy metals in the profile of these soils is the relatively high concentrations of the mobile forms of Fe and Mn in the depth horizons, due to their smoothing from the upper profile horizon and an additional supply with groundwater. On the other hand, although a stratification of the alluvial soil profile persists, there is a general pattern of heavy metal distribution, reflected by a reduction of Mn, Cu, Pb, Ni, Cd and growth content of Zn, Co, Cr, Fe from top to bottom, with 3 accumulation maxima: biogenic, gleyic and carbonatic. The typical alluvial soils investigated are not polluted with heavy metals: their concentration in the soil does not exceed the maximum permitted limits for soils of the Republic of Moldova. Under the conditions of proper management, the alluvial soils can be productive for a wide range of types of crops for dry farming, but, due to the dry climate without irrigation, the 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 cultivation. The results regarding the heavy metal content can be used to elaborate the measures and recommendations regarding the sustainable use, protection and improvement of the alluvial soils quality in the Medial Dniester meadow.

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