STUDIES ON TRANSFORMATION OF HEAVY METALS IN ERODED CARBONATIC CHERNOZEMS

STUDII ASUPRA TRANSFORMĂRII METALELOR GRELE ÎN CERNOZIOMURI CARBONATICE ERODATE

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Abstract. *It presents the results concerning the content and transformation of chemical forms of Co, Ni, Cu, and Zn in eroded carbonatic chernozems. The total content of heavy metals is directly proportional to the soil erosion degree. The transformation of chemical forms of heavy metals in eroded soils depends on the quantity of organic matter, carbonates, Fe-Mn oxides and clay minerals.*
Key words: eroded soils, heavy metals, content, transformation

Rezumat. *Sunt prezentate rezultatele cercetării conținutului şi transformării formelor chimice ale Co, N, Cu, Zn in cernoziomurile carbonatice erodate. Conținutul total al metalelor grele este direct proporțional cu gradul de erodare al solurilor. Transformarea formelor chimice a metalelor grele depinde de conținutul cantitativ al materiei organice, carbonaților, oxizilor Fe-Mn şi mineralelor argiloase din sol.*
Cuvinte cheie: soluri erodate, metale grele, conținut, transformare

INTRODUCTION

Environmental pollution is one of the most pressing problems. Avoid it completely is impossible, because pollution is a consequence of the functioning of our society, however, be able to assess, predict and deal with negative consequences is possible. A special group of polluting elements constitute the heavy metals (Co, Ni, Cu, Zn, etc.), which have the highest rates of pollution and toxicity. In view of his position, the characteristics of the composition and structure of the soil plays the regulator role of geochemical cyclic of mass flows of heavy metal. Their regulation is a combination process of migration, transformation and accumulation in the soils. To understand the mechanisms of the behavior of the heavy metals in soils and establishment the true criterion of toxicity not sufficient to determine only their total content. There is an objective necessity in the differentiation of their chemical forms, depending on soil properties and its ability to keep the metals in the absorbed state.

To assess the migratory ability of heavy metals in the food chain should take into account not only the chemical forms of metals, but also their transformation, as well as the ability of plants to withstand pollution. Despite to intensive research, many issues of absorption and transformation of heavy metals in soils remain unresolved, and this determines the relevance of this work.

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Purpose is investigate the transformation of chemical forms of copper, zinc, cobalt and nickel in the eroded carbonatic chernozems; determine the effect of carbonates and humus on the transformation of heavy metals in the soils.

MATERIAL AND METHOD

Soils subject to researches are chernozems calcareous from chain (slope) with different degree of erosion: none eroded, weakly eroded, moderately eroded, strongly eroded and accumulative (deluvial) soils. The diluvial soils include the soils formed as a result of pedolit deposits accumulation from slops in rapidly erosion processes.

Determination of heavy metals in soil samples was performed by atomic absorption spectrophotometer methods. The total (global) content of heavy metals was determined by the classical decomposition with hydrofluoric acid in combination with sulfuric acid. The chemical forms of heavy metals in soils were determined in different solutions:

- Mobile and accessible forms – ammonium acetate at pH 4,8;
- Forms from compounds with organic matter – 0,1n NaOH;
- Forms from compounds with carbonates – 1n HCl;
- Forms from compounds with Fe-Mn oxides – Mehra Jackson method;
- Forms from compounds with primary minerals: the difference between the total content of the element and its content in 20% HCl solution after incineration at 500 tºC;
- Forms from compounds with clay minerals: the difference between the content in 20% HCl solution after incineration at 500 tºC and sum content of forms with organic matter, oxides and carbonates.

RESULTS AND DISCUSSIONS

Eroded soils in Republic of Moldova occupy 80% of the total agriculture area and are most vulnerability to degradation processes. Losses of organic matter and nutrients from eroded land are considerable and have become an environmental issue for agricultural production. In result of erosion processes the weakly eroded carbonatic chernozems losses about 17% of humus, moderately eroded – 30%; strongly eroded – 52% (Leah, 2010). Losses humus materials from soils on the slopes are accumulated in the bottom on the valley. In deluvial soils the content of humus consists 3,4% (table 1).

The content of carbonates in the investigated soils show that erosion processes increased their quantity in dependence of erosion degree. The content of carbonates increased in strongly eroded soil in 6 times. A significant content of carbonates are accumulated in deluvial soil – 3,4% (table 1).

Research concerning the content of trace elements in soils has developed lately as to verify the available content for plants (studies in agrochemistry) and total determination in biogeochemical aims. Other chemical forms of trace elements in soils and their transformation under degradation factors were not studies. In the table 2-5 are presented the results of determination the amount and chemical forms of Co, Ni, Cu, Zn in eroded carbonatic chernozems.

Table 1

The content of humus and carbonates in calcareous chernozems

Depth, cm	Non eroded	Weakly eroded	Moderately eroded	Strongly eroded	Deluvial soil
Humus, %					
0-10	3,84	3,17	2,70	1,85	3,41
10-20	3,19	3,10	2,65	1,75	3,34
20-30	3,11	2,88	2,10	1,23	2,75
30-40	3,00	2,64	1,45	0,81	2,85
40-50	2,45	1,99	1,05	0,76	3,96
50-60	2,10	1,45	0,97	0,58	3,86
60-70	1,66	1,10	0,66	0,51	3,34
70-80	1,40	0,97	0,49	0,45	2,70
80-90	1,14	0,72	0,42	0,41	2,07
90-100	0,90	0,66	0,40	0,34	1,90
$CaCO_3$, %					
0-10	1,2	2,7	4,5	6,9	2,0
10-20	1,7	2,9	4,7	7,0	2,2
20-30	1,4	3,4	6,2	9,2	2,5
30-40	3,1	6,1	10,9	10,5	1,5
40-50	4,7	8,6	12,5	11,4	1,8
50-60	4,8	10,	13,8	11,1	1,5
60-70	6,3	12,2	14,7	10,9	2,3
70-80	10,2	11,4	15,4	11,4	2,0
80-90	11,6	11,3	12,3	9,9	5,0
90-100	12,1	14,0	12,1	9,1	6.0

The total content of heavy metals in eroded calcareous chernozems. The total content of elements includes all forms of chemical elements in soil, inclusively: available for plants and currently inaccessible for plants. Their accumulation in surface horizons is the result of different factors, but firstly the concentration in these horizons is result of bioaccumulation and contemporaneous actions. The calculation of the reserves of studies trace elements in the eroded carbonatic chernozems shows that their content in humic horizons is below that the average concentrations for chernozems (Leah, 2005a, 2005b).

Losses of heavy metals expressed in total forms consists in strongly eroded soils: Co – 18%, Zn – 31%, Cu – 35% of the total content of none eroded soil. The total content of Ni increases with erosion degree, in the non eroded soil contain 48,9 mg/kg, in strongly eroded – 83,5 mg/kg, which confirm that a quantity of Ni is associated primary and secondary minerals of soil (table 2-5).

Chemical forms of heavy metals in agricultural soils are studies more intensively nowadays. Studies in this context are reduced to the following. Soil components involved in the absorption of chemical elements are Fe-Mn oxides, organic matter, carbonates and clay minerals (Leah, 2005a, 2005b). These components are considered the important groups which influence chemical processes in soils, involved and competed with each other in absorption of elements. By trying to know these processes it brings a supplement in studies about pedogeochemical land includes in agriculture cycle.

Table 2

Content and chemical forms of Co in carbonatic chernozems, mg/kg, 0-20 cm

Chernozem carbonatic	Co total	mobile forms	Chemical forms of Co compounds with				
			carbo nates	organic matter	Fe-Mn oxides	minerals	
						clay	primary
Non eroded	21,0	0,18	2,4	0,10	13,0	3,0	2,5
Weakly eroded	19,5	0,25	2,3	0,10	14,0	2,0	2,3
Moderately eroded	18,0	0,30	2,1	0,10	15,0	1,5	1,8
Strongly eroded	17,3	0,35	2,0	0,10	17,0	1,0	1,2
Cumulative soil	19,7	0,40	3,3	0,10	19,0	9,0	1,7

Table 3

Content and chemical forms of Ni in carbonatic chernozems, mg/kg, 0-20 cm

Chernozem carbonatic	Ni total	mobile forms	Chemical forms of Ni compounds with				
			carbo nates	organic matter	Fe-Mn oxides	minerals	
						clay	primary
Non eroded	48,9	3,30	3,3	0,53	43,0	1,7	10,9
Weakly eroded	51,9	3,10	3,0	0,50	36,0	8,4	18,9
Moderately eroded	77,6	3,00	2,5	0,45	35,5	35,1	48,6
Strongly eroded	83,5	3,00	2,5	0,42	29,0	48,5	55,0
Cumulative soil	41,0	5,00	11,1	0,22	21,3	8,7	11,1

Table 4

Content and chemical forms of Cu in carbonatic chernozems, mg/kg, 0-20 cm

Chernozem carbonatic	Cu total	mobile forms	Chemical forms of Cu compounds with				
			carbo nates	organic matter	Fe-Mn oxides	minerals	
						clay	primary
Non eroded	22,7	1,75	3,8	0,42	10,6	2,7	5,7
Weakly eroded	20,8	1,54	3,7	0,25	10,2	2,5	4,8
Moderately eroded	18,1	1,32	3,3	0,23	9,2	2,4	4,0
Strongly eroded	14,7	1,00	3,0	0,21	8,3	3,2	5,5
Cumulative soil	15,0	1,00	4,0	1,00	6,5	2,0	2,4

Table 5

Content and chemical forms of Zn in carbonatic chernozems, mg/kg, 0-20 cm

Chernozem carbonatic	Zn total	mobile forms	Chemical forms of Zn compounds with				
			carbo nates	organic matter	Fe-Mn oxides	minerals	
						clay	primary
Non eroded	76.4	2,45	3,2	0,60	40,0	23,4	12,4
Weakly eroded	63,2	1,34	3,0	0,55	45,0	21,0	23,6
Moderately eroded	60,6	1,32	2,4	0,50	50,0	16,6	29,7
Strongly eroded	52,7	1,30	1,7	0,45	56,0	10,5	51,2
Cumulative soil	41,4	3,85	5,5	0,10	22,0	20,0	13,5

Mobile and plant accessible chemical forms consist in none eroded soils 0,2-3,0 mg/kg or 1-7% from total forms. Increasing erosion has led to their distribution in eroded soils, but accumulation occurs in deluvial soil as result of migration with humic matter. These forms have a proportional correlation with total content. Ions of these elements can be easily settled by sulfites, carbonates and hydroxides; as a result they are poorly mobile in the soil.

Chemical forms current inaccessible for plants are found as highly insoluble or practically insolubly salts, organic and organic-mineral compounds, primary and secondary minerals. They consist about 70-80% in the soils [1]. Some of the current inaccessible forms of heavy metals may become gradually over the time inaccessible for plants by physical, chemical and biochemical processes of mobilization from heavy soluble to easily soluble, ionic forms (as chemical forms associated with carbonates, organic matter, Fe-Mn oxides). They constitute potential of mobilized reserves. But, insoluble salts and crystal lattices of minerals are nutrients locked in accessible positions which constitute immobilization reserves of chemical elements (chemical forms related to primary minerals).

Chemical forms associated with carbonates. The carbonates are a common component of soils where evaporation prevails over the amount of rainfall. Thus Ca^{++} is a cation which is found in soil solution. The most widespread and mobile form of calcium carbonate in soils is calcite, which has a high dispersion and action very much the soil acidity, therefore, and the behavior of trace elements in soils. Thus, the chemical elements can be sediment by carbonates. Chemical forms associated with carbonates consists 2,4-3,8 mg/kg. There is a proportional decreasing of these forms with the degree of erosion. In the deluvial soils these forms consists up 13 to 27% from total forms. Chemical forms of the carbonates compounds forming in chernozems average 5-25% of the total. The increase in carbonate content of the soil leads to more stable fixation of heavy metals by reducing their accumulation in the metabolic forms of sorption of carbonates and Fe-Mn oxides.

Chemical forms associated with organic matter. The organic matter contained in different links all necessary plant nutrients. Ability of organic compounds associated the helatic chemical elements is know before. Most organic compounds formed soluble and insoluble complexes and this association maintenance capacity of the elements in the soil solution that depends on the nature and amount of soil organic matter. Formation of organic complexes has significant practical importance for managing biological accessibility and migration of elements in the soil. The content of heavy metals associated with organic matter is reduced, due to the increasing degree of humus mineralization. Content of heavy metals associated with organic compounds make up 0,1 to 0,8 mg/kg in the 0-20 cm horizon of carbonatic chernozems or 0,4 to 1,8% of the total content. The cumulative soil have from 0,1 to 0,2 mg/kg of these forms. In the deluvial soils can accumulate other forms organically and mineral compounds in result of increasing the content of soil carbonates.

<u>*Chemical forms associated with oxides of Fe-Mn.*</u> Soils oxides are specific components of the soil and have important meaning in retaining of trace elements in soils. A considerable amount of heavy metals is always adsorbed Fe-Mn oxides. Chernozems calcareous none eroded contain 11-13 mg/kg of Co and Cu; 40-43 mg/kg Ni and Zn associated by oxides. With erosion degree the content of these forms increase for Co, Zn, and decrease for Cu, Ni. In deluvial soil these forms do not accumulated.

<u>*Chemical associated with clay (secondary) and primary minerals.*</u> All mineral of soil have capacity to adsorption the elements ions in solution, especially in soils with high mineral content. Clay minerals in the soils are the most important mineral. Though high dispersion degree and physical-chemical characteristics clay minerals are the most active fraction of mineral soil as natural and ecological factors. Together with humus, these minerals form clay-humic soil complex. Therefore, a considerable amount of heavy metals is always associated with clay minerals. The chemical forms of Co, Ni, Cu associated in clay minerals consist in none eroded soil about 1,7-3,0 mg/kg; Zn – 23 mg/kg. Most of primary minerals can associate heavy metals in the forms inaccessible for plants that are most resistant forms in the soils, the content is 2,5-10,9 mg/kg.

The features transformation of the compounds of heavy metals in soils can be used to assess the environmental impact of anthropogenic emissions to the environment. The established mechanisms of interaction of heavy metals with soil components may serve to develop effective methods of remediation of contaminated of eroded soils.

CONCLUSIONS

1. Absorption and transformation of compounds of heavy metals in eroded soils depends on the composition of metals, as well as the properties of the soil. In the eroded soils the distribution of heavy metals on fractions of the compounds changes that can serve as a diagnostic criterion in determining of pollution.

2. Under contamination the accumulation of heavy metals in plants may be reduced due to antagonism of compounds and functioning of physiological and biochemical barriers. Carbonates in the soil contribute to the fixation of heavy metals by reducing the content of their exchange forms of sorption on the surface of the carbonates and increase adsorption capacity Fe-Mn oxides.

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