Table 6

Impact of the compositions of the hydrolytic residue on the indicators of chernozem solonets fertility. Field experiment

Variant	pH	$CaCO_3$	Humus	$N\text{-}NO_3$	P_2O_3	K_2O
		%		mg/100g soil		
	The contents in the 0-20 layer					
Control (without residues)	7.9	1.5	3.72	0.8	3.8	65.1
BM, 100 +gypsum,10	7.6	1.7	4.15	1.3	4.5	78.0
HL,50 +HS,50+gypsum,10	7.3	1.6	4.26	0.8	3.9	71.1
HS,50 +DM,50	7.5	1.7	4.33	1.1	4.5	70.0
HL,25+HS,25 +US,50	7.3	1.3	4.33	1.1	4.3	60.8
HL,25 +HS,25 +DM,50	7.6	2.1	4.23	1.2	4.3	61.3
HL,10 +HS,10+ US,30+DM,50	7.5	2.5	4.18	1.1	5.4	68.9
LD, 5%	0.2	1.3	0.35	0.1	0.4	6.8

The experimental compositions contributed to the increase of humus in the chernozem solonets. In the ploughed layer, the contents of humus increased by 0.43-9.61 % of the soil mass compared to 3.72 % in the control variant. At the same time, the contents of the mobile forms of the nutritive elements also increased. The average value in the three years of the nitric hydrogen in the 0-20 cm layer, for example, in the variant treated with hydrolytic lignin mixture, 25t + hydrolytic slime, 25 t + defecation mud, 50 t/ha constituted 12.2 me/100 g, while in the control variant this indicator was of 0.8 me/100 g of soil. An exception was observed in the variant treated with hydrolytic residues and gypsum, where the concentration of nitrates in soil was maintained at the level of the control variant. This effect is caused by the fact that the hydrolytic lignin and gypsum does not favor the nitrification process [4, 5].

We emphasize that the solonets of the experimental field contained increased quantities of mobile phosphorus and changeable potassium. The high contents of mobile phosphorus is explained by the previous fertilization with phosphorus fertilizers of these soils that were in the agricultural circuit. Though the contents of mobile phosphorus was high (3.8 me/100 gr) in the experimental compositions, an essential increase of mobile phosphorus by 0.5-1.6 mg/100 g of soil was stated.

Conclusion

The compositions of hydrolytic residues with urban sludge and defecation mud proved to be more efficient on the chernozem solonets than their separate application. When used in mixtures, the residues become more complex concerning the fertile elements that they contain, thus obtaining a multilateral impact on the soil fertility. Simultaneously the unfavorable parameters, which each separate residue has, are eliminated. In the variants with mixtures, the ameliorative action of organic residues increased by the optimization of the solonets reaction, the calcium and other elements' mobility. The experimental compositions contributed to the increase of humus contents and of the mobile forms of the nutritive elements in the chernozem solonets.

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ASSESSMENT OF MICROELEMENTS SOIL POLLUTION WITH ECOLOGICAL INDICATORS

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Abstract: Trace elements soil pollution leads to degradation of structure and aggregates stability which promotes the soil erosion and compaction. For more efficient management of the results on the content of trace elements in eroded soils the ecological indicators for characterization the accumulation in genetic horizons are used. The data confirms the soil pollution by erosion, the losses of humus, carbonates, and trace elements in arable carbonatic chernozems of catena. The humus losses in eroded soils consists 52%, the trace elements - 33-35%.

Keywords: trace elements, ecological indicators, chemical forms, soil erosion, chernozem.

Introduction

The eroded soils of Moldova constitutes about 80% from total soil surfaces [1]. On the catena with eroded soils exists the soil pollution by erosion, by excess or deficiency of plant nutrients, by soil compaction [2-7]. These soils are most vulnerable at degradation processes. The losses of humus, macro- and microelements in agricultural soils on the slopes are very considerable and become an ecological problem for agricultural production. The investigation on this research field was development in direction to verify the content of trace microelements accessible for agricultural plants and to determinate the total forms in biogeochemical aims. On the bases of these researches were developed the ecological indicators for assessment of microelement soil pollution in results of erosion degradation.

Methodical part

The investigation of catena carbonatic chernozems are presented by all degree of erosion: none eroded, weakly eroded, moderate eroded, strongly eroded and deluvial (accumulative) soil. The catenary's soils is presented by the sequence of soils with approximate age, formed on the same parental material in similar climatic conditions, but having a different characteristics in dependence of erosion degree. The soil samples were collected from all genetically horizons. The trace elements in soil samples were determinate by atomic absorption spectrophotometer, AAS-1. The total forms of microelements were determinate through classic methods of desagregations with hydrofluoric acid in combination with sulfuric acid. The chemical forms of microelements were determined in different regents.

Results and discussion

The microelements accumulation in humus horizons of soils is the results of different factors influence. However, in the first, the concentration of them in these horizons is result of bioaccumulation and actual anthropogenic pressing. The content of humus in eroded soils was in direct dependence of soil erosion degree. In the none eroded soil the humus content in the layer 0-10 cm consist 3,84 %, in the strongly eroded soil this content was 1,85 %. The average losses of organic matter by erosion consist 52%.

The deluvial soils from this zone incorporate the soils which formed in result of accumulation of pedolit deposits deluvial provenience in a very rapid temp as a result of erosion intensification on the slopes with carbonatic chernozems. In deluvial soils the content of humus has a stratification character of accumulation in superficial stratum, which depended of erosion manifestation. The some quantity of organic matter was washing from slope and deposited in the valley down. In accumulative soil the content of organic mater was same as in non eroded soils – about 3%. In the eroded chernozems the content of carbonates was changed considerable. In none eroded its content - about 1% in arable stratum (0-30 cm), in the strongly eroded – 7%, with a large values in depth, horizon C – 11%.

Copper. The total forms of trace elements include the all chemical forms from soils, inclusive: accessible for plants and actual inaccessible for plants. The distribution of Cu in soils is conditioned by following factors: parental rocks, soil genesis and erosion process. The accumulation of Cu in humic horizons depends of erosion intensity [2,4]. The total forms of Cu in humus layer of carbonatic chernozem none eroded is less under average level for chernozems of Moldova *(34,6 mg/kg)* – 22,7 mg/kg, in strongly eroded chernozem – 14,7 mg/kg. The losses of Cu total forms in eroded soil consists 35%.

The content of Cu depends of value of humus that accumulated in organic matter. In the strongly eroded soil the content of Cu in surface horizon (0-20 cm) is 14, 7mg/kg. In the deluvial soil the accumulation of total Cu was less pronounced. In superficial stratums of the deluvial soil the content of Cu is 13,5-19,1 mg/kg. In the covering soil the content of total Cu is keeping on the no eroded level – 20 mg/kg. Cu total do not have accumulation varieties in depth of horizons B, BC, C of eroded soil (table 1).

Table 1

The content of trace elements in chernozems of catena, mg/kg/% from total forms

Horizon	Depth, cm	Total content	Chemical forms of trace elements associated with					
			mobile, accessible	carbonates	organic matter	Fe-Mn oxides	minerals	
							clay	primary
1	2	3	4	5	6	7	8	9
Cu - none eroded chernozem								
Ap	0-20	22,7	1,65 2,9	3,8 16,7	0,42 1,9	10,3 45,4	2,5 11,0	5,7 25,1
BC	110-140	16,2	1,50 9,3	2,9 17,9	0,25 1,5	6,8 42,0	1,2 7,4	5,1 31,5
C	140-200	17,0	1,10 1,1	2,7 15,9	0 0	6,8 40,0	1,6 9,4	5,9 34,7
Cu - weakly eroded chernozem								
Ap	0-20	20,8	1,5 4,8	3,7 17,8	0,25 1,2	10,6 51,0	2,5 12,0	4,8 23,1
BC	90-110	18,3	1,0 5,0	3,4 18,6	0,21 1,1	6,8 37,2	7,9 43,2	8,5 46,4
C	110-180	17,6	1,0 5,7	2,4 13,6	0 0	6,5 36,9	1,1 6,3	7,6 43,2
Cu - moderate eroded chernozem								
ABp	0-20	18,1	1,3 5,5	3,3 18,2	0,25 1,4	9,2 50,8	2,4 13,3	4,0 22,1
BC	60-90	15,0	1,0 6,7	3,0 20,0	0,20 1,3	7,3 48,7	4,5 30,0	6,7 44,7
C	90-170	12,0	1,0 8,3	3,0 25,0	0 0	6,1 50,8	2,9 14,2	2,0 16,7
Cu - strongly eroded chernozem								
Bp	0-20	14,7	1,0 6,8	3,0 20,4	0,21 1,4	8,3 56,5	3,2 21,8	5,5 37,4
BC	40-60	13,7	1,0 7,3	3,0 21,9	0,20 1,5	5,5 40,1	5,0 36,5	2,6 19,0
C2	110-160	11,6	1,0 8,6	2,2 19,2	0 0	7,3 62,9	2,1 18,1	1,5 12,9
Zn - none eroded chernozem								
Ap	0-20	76.4	2,4 3,1	3,2 4,2	0,4 0,52	45,0 58,9	21,0 27,5	12,4 16,2
BC	110-140	39.3	2,2 5,6	6,5 16,5	0,3 0,76	38,0 96,7	1,3 3,3	14,3 36,4
C	140-200	48.1	2,6 5,4	1,7 3,5	0 0	35,0 72,8	13,1 27,2	23,1 48,0
Zn - weakly eroded chernozem								
Ap	0-20	63,2	1,3 2,1	3,2 5,1	0,6 0,95	56,0 88,6	23,4 37,0	51,2 81,0
BC	90-110	36,6	1,7 4,6	1,7 4,6	0,3 0,82	35,0 95,6	1,6 4,4	11,6 31,7
C	110-180	42,7	1,6 3,7	1,7 4,0	0 0	33,0 77,3	9,7 22,7	9,7 22,7
Zn - moderate eroded chernozem								
ABp	0-20	60,6	1,3 2,1	2,4 4,0	0,45 0,74	50,0 82,5	10,6 17,5	23,6 38,9
BC	60-90	68,0	1,3 1,9	1,7 2,5	0,30 0,44	50,0 73,5	16,0 23,5	45,0 66,2
C	90-170	43,8	1,3 3,0	1,7 3,9	0 0	35,0 79,9	7,1 16,2	23,8 54,3

Continuation of the table 1

1	2	3	4	5	6	7	8	9
Zn - strongly eroded chernozem								
Bp	0-20	52,7	1,3 2,5	1,7 3,2	0,55 1,04	40,0 75,9	10,5 19,9	29,7 56,4
BC	40-60	47,9	1,3 2,7	1,7 3,5	0,30 0,63	35,0 73,0	10,9 22,8	19,9 41,5
C2	110-160	42,2	1,3 3,1	1,7 4,0	0 0	35,0 82,9	5,5 13,0	22,2 52,6
Ni - none eroded chernozem								
Ap	0-20	48,9	3,0 6,1	3,3 6,7	0,5 1,02	43,0 88,0	1,7 3,5	10,9 22,3
BC	110-140	56,0	6,0 10,7	2,5 4,5	0,4 0,7	36,0 64,0	13,5 24,1	23,0 41,0
C	140-200	56,7	5,3 9,3	2,5 4,4	0 0	29,0 51,0	25,2 44,4	26,7 47,0
Ni - weakly eroded chernozem								
Ap	0-20	51,9	3,0 5,8	2,5 4,8	0,5 0,96	36,0 69,0	8,4 16,2	18,9 36,0
BC	90-110	52,2	4,0 7,7	2,5 4,8	0,4 0,77	34,0 65,0	11,7 22,4	20,2 39,0
C	110-180	44,8	4,0 8,9	2,7 6,0	0 0	36,0 80,0	6,1 13,6	9,8 22,0
Ni - moderate eroded chernozem								
ABp	0-20	77,6	3,0 3,9	3,0 3,9	0,4 0,52	35,5 46,0	35,1 45,2	48,6 63,0
BC	60-90	64,6	4,3 6,7	2,5 3,9	0,3 0,46	36,0 56,0	23,1 35,8	34,6 54,0
C	90-170	62,3	3,5 5,6	2,9 4,7	0 0	33, 53,0	26,4 42,4	34,3 55,0
Ni - strongly eroded chernozem								
Bp	0-20	83,5	3,0 3,6	2,5 3,0	0,35 0,42	29,0 35,0	48,5 58,1	55,0 66,0
BC	40-60	75,0	3,5 4,7	2,5 3,3	0,30 0,40	29,0 39,0	40,5 54,0	42,0 56,0
C2	110-160	90,6	3,0 3,3	2,5 2,8	0 0	36,0 40,0	52,1 57,5	62,6 69,0
Co - none eroded chernozem								
Ap	0-20	21,0	0,18 0,86	2,4 11,4	0,10 0,48	13,0 61,9	3,0 14,3	2,5 11,9
BC	110-140	15,0	0,40 2,67	2,3 15,3	0,10 0,67	10,4 67,3	1,2 8,0	1,0 6,7
C	140-200	19,5	0,44 2,26	2,0 10,3	0 0	14,0 71,8	1,0 5,1	2,5 12,8
Co - weakly eroded chernozem								
Ap	0-20	19,5	0,25 1,28	2,1 10,7	0,10 0,51	14,0 71,8	1,0 5,1	2,3 11,8
BC	90-110	15,8	0,43 2,72	2,2 13,9	0,10 0,63	12,0 75,9	1,0 6,3	0,5 3,2
C	110-180	13,3	0,50 3,75	2,1 15,8	0 0	9,7 72,9	1,0 7,5	0,5 3,8
Co – moderate eroded chernozem								
ABp	0-20	18,0	0,25 1,39	2,1 11,7	0,10 0,56	13,0 72,2	1,0 5,6	1,8 10,0
BC	60-90	15,7	0,47 3,00	2,2 14,0	0,10 0,64	11,1 72,6	1,0 6,4	1,0 6,4
C	90-170	14,1	0,44 3,12	2,1 14,9	0 0	10,0 70,9	1,0 7,1	1,0 7,1

Continuation of the table 1

1	2	3	4	5	6	7	8	9
Co - strongly eroded chernozem								
Bp	0-20	17,3	0,35 2,02	2,0 11,6	0,10 0,58	13,0 75,1	1,0 5,8	1,2 6,9
BC	40-60	14,6	0,50 3,40	2,1 14,4	0,10 0,68	10,4 71,2	1,0 6,8	1,0 6,8
C2	110-160	11,7	0,51 4,36	2,1 17,9	0 0	8,0 68,4	1,0 8,5	0,6 5,1

The concentration of mobile and accessible forms of Cu was in limits 3-9% from total forms. In none eroded soil these forms have less content in humus horizon – 0,65mg/kg (2,9% from total forms). In depth the concentration increase to 9,3% in horizon BC. In strongly eroded soil this dependence does not keep, the mobile forms are 7-8% from total Cu. In deluvial soil the distribution of mobile forms of Cu was in I-VI stratums of soil 7,4-5,2%; in covering soil 4,9-7,3% from total Cu.

Zinc. The distribution of total Zn has been showed in table 1. In comparison with copper Zn have another distribution in soils profile. In none eroded soil the total Zn decrease from surface (0-20 cm) – 76,4 mg/kg to 27,8 mg/kg. The content of total Zn is more in strongly eroded soil, than in none eroded. The high concentration of Zn was accumulation on the geochemical barrier, when the concentration of carbonates is bigger. The losses of total Zn in 0-20 cm stratum of soil consist 33%.

The mobile forms of Zn in nonoe eroded soil consist in 0-40 cm layer of soil 3,1-4,5% from total forms. The high accumulation of mobile Zn takes place in horizon Bh, which are the barrier of transit of parental rock – 14,4%. In other horizons (BC, Ck) the mobile forms are about 5%. In the soil with strongly erosion the concentration of mobile forms have values about 3% in whole horizon. In the deluvial soil the accessible forms of Zn have bigger limits (5-13%) then in eroded soils. The higher concentration were accumulated in humic (9,2%) and carbonatic horizons (12,9%).

Cobalt. The reserves of total Co in investigation soils are under average level (20 mg/kg) for chernozems. The arable horizons to posses the higher degree of Co content, than inferior layers. The losses of total Co consist 5% in stratum of eroded soil 0-20. The carbonatic horizon of none eroded soil has about 20 mg/kg Co. This quantity of Co does not retain in eroded soil, it consists 12 mg/kg and another quantity was migrated after 200 cm of soil.

The content of total Co in accumulative soil from valley has stratification character in distribution in dependence of different texture and humus degree. Deluvial soil content in 0-7 cm – 19,7 mg/kg Co, with a little degree in depth – to 10 mg/kg. This distribution show that Co has leached in inferior stratums (B, Ck – 11-12 mg/kg) and accumulated in covering humic horizon (20 mg/kg Co).

The mobile and accessible forms of Co consists from 0,86% to 4,36% from total forms. These forms have the proportional correlation with global forms. The Co ions can be easy sediment by sulfides, carbonates and hydroxides. As a result the Co became an easy mobile element in soils. The concentration of plant accessible forms of Co maintain a little increase in 0-20 cm of soil stratum: 0,18 mg/kg in none eroded soil, 0,35 mg/kg – in eroded soil. There are emphasizing the covering horizons of deluvial soil – Ah, Bh, keeping a well correlation with total forms. The mobile forms of Co in deluvial soil consists 4,3% from global Co. In function of investigation methods the sufficient limits of Co supply for agricultural soil is 0,5 mg/kg [7]. The exanimate eroded soils is situated under supply limits with Co for plants.

Nickel. The carbonatic none eroded chernozem has in 0-20 cm stratum about 50 mg/kg Ni. In result of erosion processes the content of Ni increased to 84 mg/kg or 68% from total content. In depth of profile the total Ni has increase in both soils, but in eroded increase was significant, up to 90 mg/kg in 140-200 cm. The mobile and accessible forms of Ni consist 3-8% from global forms. The researches of chemical forms of Ni in eroded and deluvial soil it's necessary for determinate the factors which influence their comportment and are also as an ecological determinates in this soils [3,6].

The inaccessible forms of trace elements are presented by insoluble or heavy soluble salts, organically and organic-mineral compounds, primary and secondary minerals. It consists in this soil about 70-80%. The part of them can be successive in time accessible for plants through physic-chemical and biochemical processes of mobilization from insoluble to easy soluble and ionic status. These forms constitute the mobilized potential reserves of trace elements in soils. But in practically insoluble salts and in minerals are remain another part of elements which are immobilized for plants.

Ecological indicators The *degree of fixation* of trace elements by soil components showed that in the eroded soils the main role in their absorption is organic matter, oxides of Fe and Mn, clay minerals. The *transformation of chemical forms* of trace elements in soils is influenced by the action of various factors. The soil erosion increases the content of soluble forms and associated with clay minerals, decrease the forms of organic matter, oxides, and primary minerals. In non eroded, fallow, cumulative soils reduction occurs content of mobile forms, chemical forms of clay minerals compounds is reduced. The arable soils of slope show, that in according to erosion increasing, the content of chemical forms associated with carbonates and oxides is higher. *Interdependence* of trace elements, their *deficiency* and *toxicity* in the soils is important for optimal development and grow of plants. Plant has valuable information related to soil ratio of elements: Fe/Mn, Ni/Co, Zn/Cu, etc. These correlations are well highlighted, especially when there is a surplus of chemical elements in soils. Deficiency affects physiological processes and consequently on plant productivity. Diagnosis deficiency and correction methods require further research. For different plant species, the concentration, which determines the deficiency and toxicity, is very different.

Conclusion

The regularity distribution of chemical forms content of trace elements in carbonatic chernozems eroded and none eroded are coordinated by eroded degree, content of soil carbonates, oxides and clay minerals and have a good correlation with them. The mobile chemical forms of trace elements in carbonatic chernozems are partial or total submissive transformations, in this case under erosion processes. Due time this forms can be passing from one forms to another, to maintain the dynamic equilibrium, but sometimes the accessible forms are immobile. The study of chemical forms transformation of different trace elements in soils complete the information about their provenience.

Between chemical forms of microelements in soils does not exist precise separation elements, but there are transitions, gradual passing. At the separation of chemical forms its necessary to select the adequate methods of determination and stabilization the equilibrium between them for each type of soil. The other ecological problem is study the factors which influence the mobility of elements in soil and anthropogenesis. Using the humus and chemical forms of trace element its can be diagnostically the level of erosion degree and sometimes the level of pollution by erosion.

The non eroded and eroded carbonatic chernozems contain the trace elements under average level, which are tolerated by plants. The losses of trace elements through erosion consist: Cu - 35 %, Zn - 33%; Ni – 15%, Co-5%. The distribution of elements in profiles depends of organic bioaccumulation and quantity of carbonates. The agriculture soil from slope needs in fertilization with organic fertilizers. These measures will conduct to increase the content of humus and accumulation of trace elements in mobile and accessible forms for plants.

Using ecological indicators in assessing chemical pollution of soils allows gaining more knowledge on the current status and trends that occur in soils and the environment.

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