

## **HUMUS AND TRACE ELEMENTS AS AN INDICATORS OF MATERIAL ERODED FROM CARBONATIC CHERNOZEMS SURFACE**

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### **Abstract**

*A study was conducted to investigate the content of humus and trace elements (Cu, Zn, Co, Ni) in soil of catena with Calcareous (Carbonatic) Chernozems. The data obtained use as materials eroded from soils surface indicators of losses. The humus losses in eroded Chernozems are 52%, the losses of trace elements are 33-35%.*

### **INTRODUCTION**

The Calcareous (Carbonatics) Chernozems in The Republic of Moldova are about 44% from total soil surfaces (1). On the catenae with Calcareous Chernozems there is soil pollution by erosion, by excess or deficiency of plant nutrients, by compaction. These soils are most vulnerable to erosion processes. The losses of humus, macro and microelements in agricultural soils on the slope are very considerable and become an ecological problem for agricultural production. The investigation on this research field was the development to verify the content of trace microelements accessible for agricultural plants and to determine the total forms in biogeochemical aims. This article presents the data that confirm soil pollution by erosion, the losses of humus, carbonates and the total and mobile forms of Cu, Zn, Co and Ni in the Calcareous Chernozems on the catena.

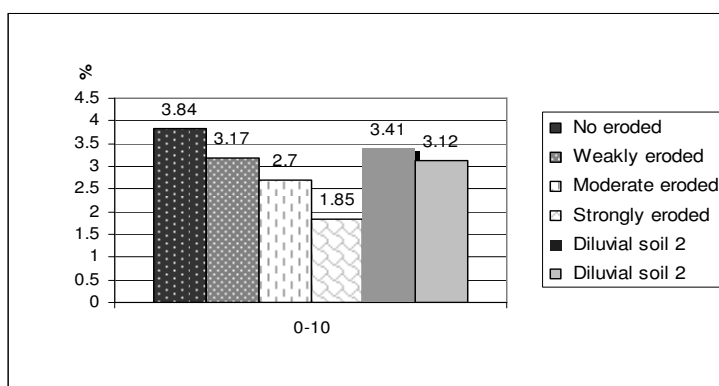
### **MATERIAL AND METHODS**

The soil investigations are Calcareous Chernozems on the catena with all types of erosion: non eroded, weakly eroded, moderately and strongly eroded and deluvial (accumulative) soil. The catenaries' soils are presented by the sequence of soils with an approximate age, formed on the same parental material in similar climatic conditions, but having different characteristics depending on the relief variety. The present paper shows the most representative soils: Chernozems non eroded (on the slope top - inter stream), strongly eroded (on the slope bottom) and deluvial soils in depression. The soil samples were collected from all the genetic horizons. The trace elements in soil samples were determined by an atomic absorption spectrophotometer - AAS1. The total forms of microelements were determined by classic methods of desegregation with hydrofluoric acid in combination with

sulfuric acid. The mobile and accessible forms were determined in  $\text{CH}_3\text{COONH}_4$  solution - pH=4.8.

## RESULTS AND DISCUSSION

The microelements accumulation in humus horizons is the result of different factors influence. However, in the first, their concentration in these horizons is the result of bioaccumulation and actual anthropogenic pressing. The content of humus in eroded soils was in direct dependence on the soil erosion degree. In the non eroded soil, the humus content in the layer of 0-10 cm of soil has 3.84%, in the strongly eroded soil this content was 1.85% (Figure 1).



**Fig. 1. Humus content in the Chernozems of catena, 0-10 cm**

The loss of organic substances by erosion was 52%. In the deluvial soils, the content of humus had the stratification character of accumulation in superficial stratum, which depended on erosion manifestation. The content of humus was washed from the slope and deposited in the valley down. In the deluvial soil, the content of organic mater was the same as in non eroded soils - about 3%. In the Chernozems from the slope, the content of carbonates was changed considerably. In non eroded soils, its content was about 1% in the arable stratum (0-30 cm), but in the strongly eroded Chernozems - 7%, with a large values in depth - 11%.

**Copper** The total forms of trace elements included all the chemical forms from soils, including: accessible for plants, actual inaccessible for plants. The distribution of Cu in soils was conditioned by the following factors: parental rocks (material), soil genesis and erosion process. The accumulation of Cu in the humus horizons depends on the intensity of bioaccumulation and anthropogenesis (3). The total forms of Cu in the humus layer of Chernozems without eroded was less under average level for Chernozems of Moldova (34.6 mg/kg) - 22.7 mg/kg, in strongly eroded Chernozems - 14.7 mg/kg. The losses of total forms Cu in eroded soil were 35% (Table 1).

*Table 1*

**Content of total and mobile forms of trace elements in Chernozems on the catena, mg/kg /% from total forms**

Horizon and depth, cm	Cu		Zn		Co		Ni	
	total	mobile	total	mobile	total	mobile	total	mobile
<b>Calcareous Chernozem - non eroded</b>								
Ap 0-20	<b>22.7</b>	<u>0.65</u> 2.9	<b>76.4</b>	<u>2.4</u> 3.1	<b>21,0</b>	<u>0.18</u> 0.9	<b>48.9</b>	<u>3.0</u> 6.1
Ah 20-40	<b>18.4</b>	<u>0.90</u> 4.9	<b>55.5</b>	<u>2.5</u> 4.5	<b>17,5</b>	<u>0.15</u> 0.9	<b>50.0</b>	<u>3.0</u> 6.0
Bh 40-110	<b>14.1</b>	<u>1.10</u> 7.8	<b>27.8</b>	<u>4.0</u> 14.4	<b>15,0</b>	<u>0.40</u> 2.7	<b>54.1</b>	<u>6.8</u> 12.6
BC 110-140	<b>16.2</b>	<u>1.50</u> 9.3	<b>39.3</b>	<u>2.2</u> 5.6	<b>15,0</b>	<u>0.40</u> 2.7	<b>56.0</b>	<u>6.0</u> 10.7
C 140-200	<b>17.0</b>	<u>1.10</u> 6.4	<b>48.1</b>	<u>2.6</u> 5.4	<b>19,5</b>	<u>0.44</u> 2.3	<b>56.7</b>	<u>5.3</u> 9.3
<b>Calcareous Chernozem strongly eroded</b>								
Bp 0-20	<b>14.7</b>	<u>1.0</u> 6.8	<b>52.7</b>	<u>1.3</u> 2.5	<b>17.3</b>	<u>0.35</u> 2.0	<b>83.5</b>	<u>3.0</u> 3.6
Bh 20-40	<b>14.8</b>	<u>1.0</u> 6.8	<b>48.8</b>	<u>1.3</u> 2.7	<b>16.9</b>	<u>0.40</u> 2.4	<b>72.6</b>	<u>4.0</u> 5.5
BC 40-60	<b>13.7</b>	<u>1.0</u> 7.3	<b>47.9</b>	<u>1.3</u> 2.7	<b>14.6</b>	<u>0.50</u> 3.4	<b>75.0</b>	<u>3.5</u> 4.7
C1 60-110	<b>12.6</b>	<u>1.0</u> 7.9	<b>67.7</b>	<u>1.3</u> 1.9	<b>14.3</b>	<u>0.44</u> 3.1	<b>69.6</b>	<u>4.6</u> 6.6
C2 110-160	<b>11.6</b>	<u>1.0</u> 8.6	<b>42.2</b>	<u>1.3</u> 3.1	<b>11.7</b>	<u>0.51</u> 4.4	<b>90.6</b>	<u>3.0</u> 3.3
<b>Deluvial Calcareous Soil</b>								
I 0-7	<b>13.5</b>	<u>1.0</u> 7.4	<b>31.3</b>	<u>4.0</u> 12.8	<b>19.7</b>	<u>0.40</u> 2.0	<b>41.0</b>	<u>5.0</u> 12.2
II 7-19	<b>16.2</b>	<u>1.0</u> 6.2	<b>51.5</b>	<u>3.5</u> 6.8	<b>13.2</b>	<u>0.40</u> 3.0	<b>49.5</b>	<u>3.5</u> 7.1
III 19-30	<b>18.6</b>	<u>1.0</u> 5.4	<b>44.0</b>	<u>5.0</u> 11.4	<b>10.9</b>	<u>0.40</u> 3.7	<b>54.3</b>	<u>2.0</u> 3.7

IV 30-45	<b>14.5</b>	<u>1.0</u> 6.9	<b>49.0</b>	<u>5.0</u> 10.2	<b>10.2</b>	<u>0.40</u> 3.9	<b>53.3</b>	<u>3.5</u> 6.6
V 45-56	<b>16.3</b>	<u>1.0</u> 6.1	<b>36.3</b>	<u>5.0</u> 13.8	<b>10.7</b>	<u>0.50</u> 4.7	<b>46.2</b>	<u>3.5</u> 7.6
VI 56-69	<b>19.1</b>	<u>1.0</u> 5.2	<b>41.2</b>	<u>2.3</u> 5.6	<b>10.5</b>	<u>0.50</u> 3.8	<b>45.4</b>	<u>3.5</u> 7.7
A 69-100	<b>20.6</b>	<u>1.0</u> 4.9	<b>43.7</b>	<u>4.0</u> 9.2	<b>19.9</b>	<u>0.51</u> 2.6	<b>42.9</b>	<u>5.5</u> 12.8
AB 100-130	<b>20.4</b>	<u>1.0</u> 4.9	<b>49.7</b>	<u>2.3</u> 4.6	<b>11.0</b>	<u>0.50</u> 4.5	<b>47.7</b>	<u>5.0</u> 10.5
B1 130-160	<b>19.3</b>	<u>1.0</u> 5.2	<b>49.6</b>	<u>2.3</u> 4.6	<b>11.0</b>	<u>0.40</u> 3.6	<b>48.8</b>	<u>3.5</u> 7.2
B2 160-220	<b>20.2</b>	<u>1.0</u> 5.0	<b>32.6</b>	<u>4.2</u> 12.9	<b>11.7</b>	<u>0.45</u> 3.8	<b>47.9</b>	<u>5.3</u> 11.1
B3 220-250	<b>18.1</b>	<u>1.0</u> 5.5	<b>42.6</b>	<u>3.7</u> 8.7	<b>12.0</b>	<u>0.35</u> 2.9	<b>54.0</b>	<u>4.0</u> 7.4
Bck 250-280	<b>17.4</b>	<u>1.0</u> 5.7	<b>41.3</b>	<u>3.8</u> 9.2	<b>11.5</b>	<u>0.40</u> <u>3.5</u>	<b>44.5</b>	<u>4.0</u> 9.0
Ck 280-430	<b>13.7</b>	<u>1.0</u> 7.3	<b>38.2</b>	<u>4.1</u> 10.7	<b>11.3</b>	<u>0.41</u> 3.6	<b>45.2</b>	<u>3.8</u> 8.4

The content of Cu depended on the value of humus, the Cu was accumulated in organic matter. In the strongly eroded soil, the content of Cu in surface horizon (0-20 cm) was 14.7 mg/kg. In the deluvial soil, the accumulation of total Cu was less obvious. In I-VI stratum, the content of Cu was 13.5-19.1 mg/kg. In the covering soil, the content of total Cu was kept at the non eroded level - 20 mg/kg. Total Cu did not have accumulation varieties in depth of horizons B, BC, C of eroded soil.

The concentration of mobile and accessible forms of Cu was in limits 3-9% from total forms. In non eroded soil, these forms had less size in humus horizon – 0.65 mg/kg (2.9%). In depth the concentration increased to 9.3% in horizon BC. In the strongly eroded soil this dependence was not present, the mobile forms were 7-8% from total Cu. In the deluvial soil, the distribution of mobile forms of Cu was in I-VI stratum of soil 7.4-5.2%; in covering soil 4.9-7.3% from total Cu.

**Zinc** In comparison with copper, Zn had another distribution in the soil profile. In the non eroded soil, the total Zn decreased from surface (0-20 cm) - 76.4 mg/kg to 27.8 mg/kg.

The content of total Zn was higher in the strongly eroded soil, than in the non eroded. The high concentration of Zn was accumulated on the geochemical barrier,

when the concentration of carbonates was higher. The losses of total Zn in 0-20 cm stratum of soil were 33%.

The mobile forms of Zn in the non eroded soil consisted in 0-40 cm layer of soil 3.1-4.5% from total forms. The high accumulation of mobile Zn took place in Bh, which were the barrier of transit of parental rock - 14.4%. In other horizons (BC, Ck) the mobile forms are about 5%. In the soil with strong erosion, the concentration of mobile forms had values about 3% in the whole horizon. In the deluvial soil, the accessible forms of Zn had bigger limits (5-13%) than in eroded soils. The higher concentrations were accumulated in humus (9.2%) and carbonate horizons (12.9%).

**Cobalt.** The reserves of total Co in investigation soils were under the average level (20 mg/kg) for Chernozems. The arable horizons had the higher degree of Co content, than their inferior layers. The losses of total Co were 5% in stratum of eroded soil 0-20. The carbonates horizon of the non eroded soil had about 20 mg/kg Co. This quantity of Co did not retain in eroded soil, it consisted of 12 mg/kg and another quantity migrated after 200 cm of soil (2).

The content of total Co in accumulative soil from the valley had stratification character in distribution in depending on the different texture and humus degree. The deluvial soil content in 0-7 cm - 19.7 mg/kg Co, with a little degree in depth - to 10 mg/kg. This distribution showed that Co leached in the inferior stratum (B, Ck - 11-12 mg/kg) and accumulated in the covering humus horizon (20 mg/kg Co).

The mobile and accessible forms of Co varied from 0.86% to 4.36% from total forms. These forms had the proportional correlation with global forms (Table). The Co ions could be easy sedimented by sulfides, carbonates and hydroxides. As a result, the Co became a weakly mobile element in soils. The concentration of plant accessible forms of Co remained relatively high in 0-20 cm of soil stratum: 0.18 mg/kg in the non eroded soil, 0.35 mg/kg - in the eroded soil. There are emphasizing the covering horizons of the deluvial soil - Ah, Bh, keeping a good correlation with total forms. The mobile forms of Co in the deluvial soil were 4.3% from global Co. According to the investigation, the methods of the sufficient limits of Co supply for agricultural soil were 0.5 mg/kg. The examined soil has under the supply limits with Co for plants.

**Nickel.** The carbonatics no eroded Chernozem had in 0-20 cm stratum about 50 mg/kg of Ni. As a result of the erosion processes, the content of Ni increased to 84 mg/kg or 68%. In depth of profile, the total Ni has increased in both soils, but in the eroded one increase was significant, to 90 mg/kg in 140-200 cm. The mobile and accessible forms of Ni were 3-8% from global forms.

The research of the chemical forms of Ni in eroded and deluvial soil is necessary to determine the factors which influence their behaviour and are also an ecological factor in these soils (2, 4). The deluvial soils from this area incorporate the soils which formed in result of accumulation of pedolit deposits deluvial provenience

very fast temp as a result of the erosion intensification on the slopes with carbonatic Chernozems.

The inaccessible forms of trace elements are presented by insoluble or heavy soluble salts, organically and organic-mineral compounds, primary and secondary minerals and consists in this soils about 70-80%. Part of them can be successive in time accessible for plants through physical-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 there are remains another part of the elements which are immobilized for plants.

The regular distribution of the chemical forms content of trace elements in carbonatic Chernozems eroded and non eroded are coordinated by the 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. In time, these forms can pass from one form to another, to maintain the dynamics 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 the chemical forms of microelements in soils there does not exist precise separation elements, but there are transitions, gradual passing. At the separation of chemical forms, it is necessary to select the adequate methods of determination and stabilization of the equilibrium between them for each type and subtype of soil. The other ecological problem is the study of the factors which influence the mobility of elements in soil and their anthropogenesis. Using humus and chemical forms of trace element we can diagnose the level of erosion and sometimes the level of pollution by erosion.

## CONCLUSIONS

1. The Calcareous Chernozems non eroded and eroded contain the trace elements under the average level, and are tolerated by plants. The losses of trace elements through erosion are: Cu - 35%, Zn - 33%; Co - 5%. The humus losses in eroded soils are 52%.
2. The distribution of elements in profiles depends on organic bioaccumulation, quantity of carbonates. The agricultural soil from the slope is necessary in the 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.

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