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Priorities of Agroecological Monitoring of the Composition of Soil Trace Elements Taking into Account the Peculiarities of its Formation Over Time

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Abstract: The geochemical features of the chronosequences of soils in forest-steppe and steppe pedogenesis under the influence of zonal types of vegetation have been studied. A new method for the integral assessment of the biogeochemical transformation of soils in the chernozem sequence over time according to the most informative list of trace elements which are accumulated or washed away by soil solutions from humus horizons of soils was proposed. A priority list of five trace elements which is recommended for inclusion into the monitored parameters in the system of soil and environmental monitoring of agricultural land is presented. It is shown that periodic diagnostics of trace elements deficiency in agricultural lands and its correction by adding micronutrients to compensate for the loss of the most rapidly consumed trace elements is required. A priority list of chemical elements useful for plants (Ca, Zn, Mg, Ni, P, Mn) as monitoring indicators for the conditions of erosive agrolandscapes was substantiated.

Key words: Agroecological monitoring, trace elements, soil formation, product quality, chernozems, chemical

INTRODUCTION

Soil is a specific component of the biosphere, since, it acts as a natural buffer which controls the transfer of chemical elements and compounds to the atmosphere, hydrosphere and biota (Kabata-Pendias and Pendias, 1984). Soils ensure basic ecosystem functions but they are also under the pressure of human activity which in many respects has determined appreciable shifts in the efforts undertaken over the last 15 years to quantify the impact on soils (Legaz *et al*., 2017). A comprehensive assessment of the impact of the economic activity makes it possible to study the spatial-temporal patterns of transformation of agrolandscapes in the conditions of an intensive farming and to determine a rational strategy for organizing the soil and environment monitoring in space and time (Lisetskiy and Pichura, 2016). Previous studies of in the soil landscapes of the Southern Russia (Dyachenko *et al.*, 2014) testify that body height of concentration and change of ratios of chemical elements, though reflects interaction of many factors accompanying region development but anthropogenesis has decisive influence on dynamics of microcells in soils.

The task of the soil-ecological monitoring is to control assess forecast and manage the state of the main indicators of soil fertility in order to obtain high and stable crop yields of good quality as well as to prevent pollution of the natural environment. In modern conditions, the agrochemical maintenance of arable lands provides a periodic receipt of monitoring data on the content of humus, nutrients and a limited range of trace elements. For an increasing number of trace elements, their physiological and biochemical role in complex biological and physiological processes is identified. While there is an extensive special literature on the physiological and biochemical significance of essential trace elements (Mertz, 1981), the information on a number of trace elements that play a little-studied role in the soil formation and their translocation into plant organs is limited (Bol'shakov, 2002; Pardo *et al.*, 2014; Teng *et al*, 2014; Obade and Lai, 2016). Therefore, in order to characterize arable soils in the conditions of modern intensive farming, it is important to know how the clay minerals composition is formed during pedogenesis (Goleusov and Lisetskii, 2008; Lisetskii, 2012) and what transformations occur during a strong biological depletion of elements in agrocenoses.

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The purpose of our study was to study the biogeochemical features of the chronosequence of soils in the conditions of the forest-steppe and steppe during their natural reproduction and the predictive determination of deficient elements with which the finely dispersed fractions of soils are enriched.

MATERIALS AND METHODS

The objects of the study in 2013-2016 were different-aged soils (for soil horizons A and AA) and their parent rocks in the Belgorod Region. Since, the nature and rate of destruction of primary clays and the synthesis of secondary clays minerals depend to a large extent on the moisture and temperature conditions, the study was carried out for two chronosequences in the forest-steppe and steppe zones. Soil colours (dry moist) were described using the Munsell system.

The following granulometric parameters were measured on soil: the fraction <1 mm and the fraction <0.002 mm (clay content (Atterberg, 1905). Clay fraction was taken from a weighed quantity of the soil in 500 g which after adding distilled water was passed through a sieve 0.25 mm. as a suspension. The suspension was then passed through a precision woven sieve of size 0.002 mm (Fritsch). Concentration of macro and microelements within the soil and clay were determined by technique of measuring metals mass fraction and oxides in powder samples using the method of X-ray fluorescence analysis on the X-ray spectrometer (Spectroscan Max-GV). This allowed calculating the ratio $S_C/S_g=S_{<0.002mm}/S_{<1mm}$ for each of the 22 oxides, which reflects the degree of trace elements concentration in clay (S_C) as compared with the total soil content (S_g).

The estimates of the content of chemical elements in the soil and clay fraction were made by calculating the average geometric value:

$$S = \sqrt[n]{x_1 \cdot x_2 \cdot \ldots \cdot x_n} \quad (1)$$

where x_1, x_2… x_n – is the content of chemical elements. The coefficient of accumulation in clay fraction (Ka) was determined for each element by Eq. 2:

$$K_a = S_C / S_g , \quad (2)$$

Where:
S_C = Clay fraction
S_g = General soil content

To identify the most intensively accumulated chemical elements, the distribution diagrams of chemical elements were constructed according to the degree of their accumulation in clay fraction.

In addition, the assessment of the informativeness of chemical elements in the diagnostics of pedogenesis processes (Lisetskii and Chepelev, 2014) made it possible to determine a list of 16 elements that have significant differences from the parent rocks, both in relation to the concentration in the humus horizons and with respect to scattering under the influence of soil- forming processes.

RESULTS AND DISCUSSION

Geochemical transformation of the soil in relation to the parent rock: Reference soils (Holocene soils) under different type of vegetation (oak forests and meadow steppes) are in many respects geochemically similar, if this comparison is made by the ratio of elements in the humus-accumulative horizon and in the parent rock. The comparison of geochemical differences of soils from the horizon A under the oak grove and the steppe showed that the soils in the forest environment are characterized by depletion of such elements as Mg, Pb as, Na, Sr, Ca, Ti, Ni with a more active accumulation (by 30%) V and Cr.

At the early stages of weathering and soil formation, the trace elements composition in the soil as a rule is inherited from the parent rock. However, in the course of time, the trace elements composition in the soil begins to differentiate under the influence of dominant soil-forming processes (Kabata-Pendias and Pendias, 1984). Soils in relation to the earth's crust are characterized by an enrichment («1-10) in such elements as those that we studied: K, Na, Ca, Sr, Zn, Al, Ti, Si, Zr, Pb, Mn as (Speidel andAgnew, 1982).

The fate of trace elements which are mobilized during the biogeochemical transformation of the mineral part of the soil, may be determined by the possibility in certain conditions, of their sedimentation incorporation into minerals, adsorption by soil components, adsorption or absorption by organic matter but also, leaching out from the soil (Kabata-Pendias and Pendias, 1984). The concentration and diffusion of chemical elements are opposite phenomena which determine one of the important features of geochemical approaches to the study of media and their temporal states. An analysis of the average values of the ratio of the concentration of chemical elements in the Soil (Si) and in the parent rock (Pi), i.e., Si/Pi on 18 horizons (A and AB) of 12 different-aged soils in the chronosequence showed that

11 chemical elements accumulate in the humus horizons of soils (Si/Pi>l) which can be represented as a decreasing sequence: Mn>Pb>Cu = Zn>Ti = Ni = K>V = Cr = Fe = Al while 5 chemical elements are characterized by their removal: As>Sr>Na>Mg = Ca. In the conditions of the forest-steppe (with climatic parameters: the average annual temperature is +6-7 °C, the total precipitation is 550-630 mm per year (Lisetskii *et al.*, 2011)) on rocks of loamy composition, the stable elements-components of the soil system include Ti, Al, Mn, Fe, K, Ni, Cu, Pb, Cr, V, Zn while the mobile elements include Ca, Sr, Na, Mg, As. This list is substantiated as a result of comparison of geochemical features of soils with their parent rocks.

The proposed indicator of the geochemical transformation of the soil or its individual genetic horizons (ST) reflects the balance of the relative accumulation of conservative components of the soil's material composition as a result of the removal of more migratory mobile components.

Using the results of the analysis of the gross composition and the above grouping of components with respect to their mobility, the calculation of the indicator of the geochemical transformation of each soil which is a member of the chronosequence (SO) at a moment of the time (t) is proposed to be done according to Eq. 3:

$$ST_t = 100 \cdot \frac{(S_{C1}/P_{C1} \cdot S_{C2}/P_{C2} \cdot ... \cdot S_{Cn}/P_{Cn})}{(S_{L1}/P_{L1} \cdot S_{L2}/P_{L2} \cdot ... \cdot S_{Lm}/P_{Lm})} \quad (3)$$

where (C1, C2,..., Cn) are stable and (L1, L2,..., Lm) are the mobile components of the real composition in the Soil (S) and the Parent rock (P).

In the proposed list of diagnostic elements, it is important to consider their paragenous associations, since, the interaction between chemical elements may be antagonistic or synergistic and this affects the ability of plants to selectively absorb certain elements. In the course of soil formation, there takes place an increase in the thickness of the humus horizon and its humification where special interactions of organomineral complexes with the media around the plant roots are formed. With time as leaching (decalcification) of the upper horizons of soils occurs, during the synergy of calcium with Cu, Mn, Zn, there decreases the antagonism Na with such elements as Al, Fe, Co, Ni.

The complex of interrelated processes of concentration-diffusion is due to their duration and therefore as the soils develop, the value ST should increase with time. For the forest-steppe soils as the analysis has shown, it is reasonable to insert in the numerator of Eq. 3 the results of determining elements specified above. In these bioclimatic conditions, if we imagine a simulated situation of the starting conditions of pedogenesis when the transformation of the parent rock has not yet begun, the value of ST will be equal to 90. The increase of this value is possible primarily due to a decrease in the values in the denominator of Eq. 3 which will diagnose the process of eluviation, accompanied by the depletion of Ca, Sr, Mg, Na as. In particular for the chernozem sequence of soils in the conditions of the forest-steppe, it has been established that the order of diffusion of chemical elements in the increasing ranked sequence has the form: Ca<Sr<Mg<Na<As. Then, the concentration of stable components of the material composition of the soil either reflects a relative increase or exceeds the depletion.

Forecast of erosional transformation of the trace element composition of soils: The soil inherits the mineralogical composition of the parent rocks. Pedogenesis is accompanied by destruction, synthesis of minerals, migration but does not significantly change the mineralogical composition. Such factors as the composition and age of the parent rocks, the clay minerals, genetic connection, their possible mutual transformations in different geochemical settings in the soil system, largely explain the absence of strict confinement of the clay minerals to certain types of soils.

The finely, dispersed granulometric fractions of soils concentrate secondary minerals which are represented by clay minerals, minerals-salts and minerals-oxides Fe and Al. The main part of secondary minerals is clay minerals which along with humus is the main source of inputs of mineral elements into plants. Clay minerals dominate in the clay fraction of the soil (fraction of the soil solids which is less the 2 ja or 0.002 mm) of many soils which affect the physical, physical-chemical, water-physical and physical-mechanical properties of the soil (plasticity, stickiness, swelling, shrinkage, cohesion) and the soil structure and moisture retention as well.

Humus horizons of different-age soils often have a slightly alkaline reaction of solutions and have a higher content of organic matter under the steppe vegetation than under the forest (Table 1).

Of the 22 chemical elements and oxides, that were determined in the soil, only 5 macroelements and 6 trace elements were characterized by an intensive accumulation (Table 2).

On the graphs of the distribution of values E_a for each of the objects (Fig. 1), the inflection points of the curves of the change in the values were determined S_c/S_g (they were within 150-250) and on their basis the priority chemical elements with respect to the accumulation in the clay.

Table 1. Different-aged soils on archaeological sites and the Holocene analog (S4)

Soils	Time of pedogenesis, yrs	Horizon	Layer, cm	Colour (dry)	pH (H_2O)	$CaCO_3$, %	P_2O_5, mg kg^{-1}	Corg, %	<0.01 mm
Steppe conditions									
S1	368	A	0-23	10YR 4/1	7.4	2.5	0.2	3.9	36
S2	2500	A+AB	0-31	10YR 4/2.5	6.6	1.1	0.5	1.8	34
S3	3750	A	0-22	10YR 3/2	8.3	5.6	0.4	3.5	38
S4	10000	A	0-36	10YR 3/3	8.1	2.5	0.1	3.1	31
Forest steppe conditions									
FS1	73	A+AB	0-19	10YR 5/3.5	6.2	1.0	0.1	1.1	38
FS2	930	A+AB	0-26	10YR 4/2	7.3	1.2	0.9	2.2	7
FS3	2450	A+AB	0-41	10YR 5/2	7.3	2.5	1.3	2.6	31

Table 2. Chemical elements and oxides of intensive accumulation in soils

Elements	Units	S1	S2	S3	S4	FS1	FS2	FS3	Average
CaO	%	4.7	2.6	6.7	6.8	2.2	5.6	7.7	5.3
MgO	%	1.8	1.6	1.8	2.1	1.4	2.0	2.1	1.8
Na	%	1.9	1.1	1.7	1.6	1.4	1.8	1.8	1.6
P_2O_5	%	0.3	0.4	0.3	0.3	0.4	0.9	3.0	0.9
MnO	%	0.10	0.14	0.12	0.12	0.10	0.07	0.19	0.12
Sr	ppm	397.3	156.3	361.1	369.2	248.0	415.2	548.0	349.6
Zn	ppm	180.9	155.0	154.4	199.8	190.6	223.5	342.9	211.0
Ni	ppm	94.7	76.8	74.4	85.4	77.5	84.6	67.4	77.7
Cu	ppm	67.6	79.4	59.2	71.6	69.4	50.3	34.9	60.8
Pb	ppm	35.0	35.7	33.0	38.1	45.1	34.5	28.9	35.9
Fe	ppm	5.7	5.3	4.8	5.8	6.3	5.3	4.0	5.2

Our study showed that the average (n = 17) value of the ratio of the different-age soils $Si0_2:Al_20_3$ in the fraction <0.002 mm is 2.95±0.33. In soils of the chronosequence, the ratio $Si0_2:Aip_3$ in the soil is 2.25 times greater than that in the clay. And in the steppe environment, both in the soil and in the clay, the ratio $Si0_2:Al_20_3$ is less than in the forest-steppe soils (by 22 and 33%, respectively). In the general array of the objects, two groups are distinguished: the soils of which $Si0_2:Al_20_3$>2.6 (n = 9) and on the average is 3.8±0.4; The soils in which $Si0_2:Al_20_3$<2.5 (n = 8) and on the average is 2.0±0.2. The first group consists mainly of soils that were formed in the forest environment as well as newly formed soils containing more vermiculite in the clay fraction. The second group is formed by soils of long-term pedogenesis with predominance of kaolinite, illite and chlorite.

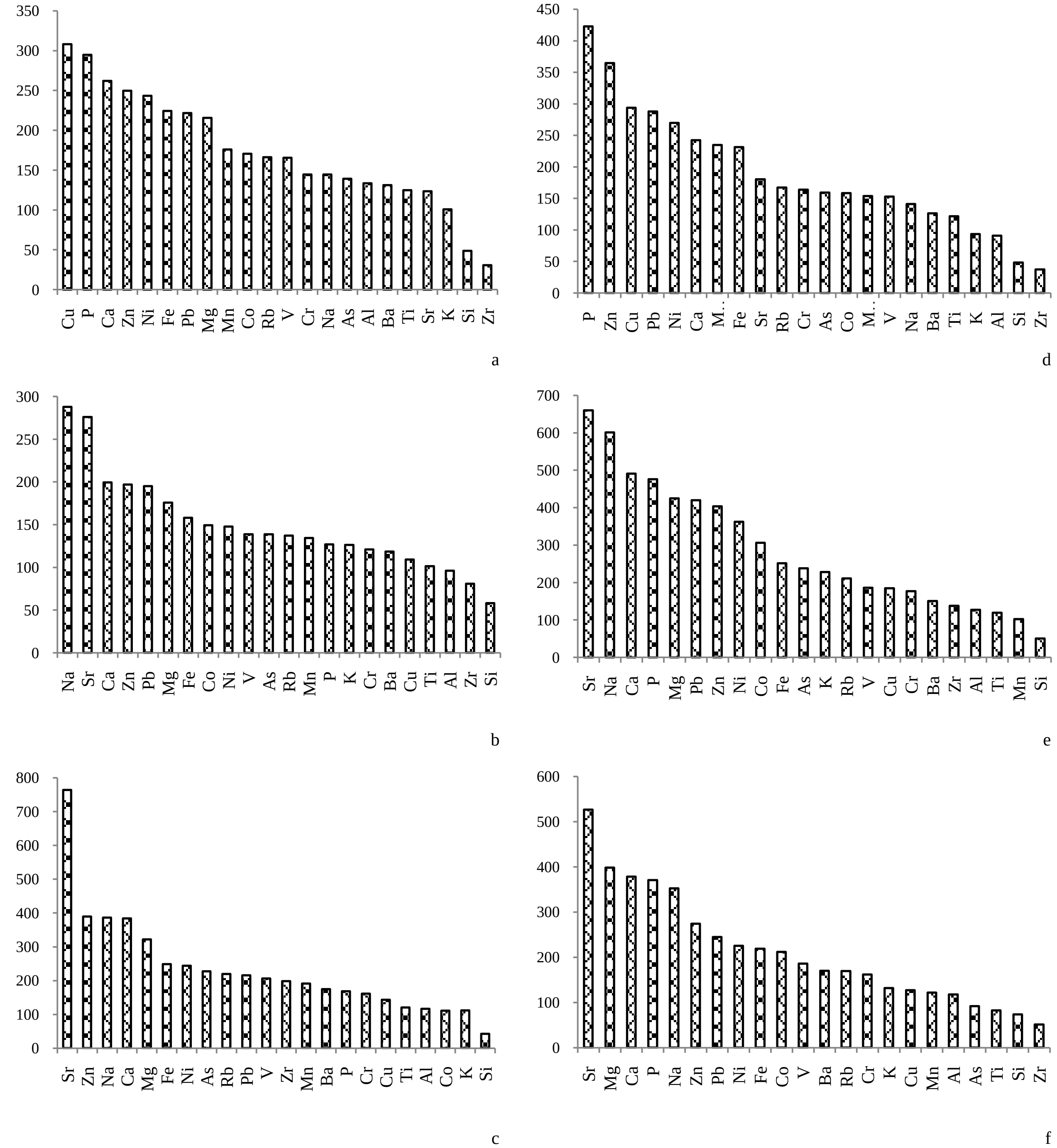
Soils that have experienced soil degradation (eroded and correspondingly, carbonate species on slopes and also, on watersheds but depleted by an intensive and/or long-term farming as a result of physico-chemical degradation (Lisetskii *et al*., 2015)) are in many respects similar in the trace element composition to the newly formed soils. Their comparison with the full-profile (Holocene) analogues allows to determine a priority list of trace elements for the monitored parameters in the system of soil-ecological monitoring of agricultural lands. But since, the sequence of biogenic accumulation of chemical elements in forest-steppe chernozem soils is the following Mn>Fe>Ni>Cu>Zn, then among the most vulnerable trace elements, due to a more active depletion in the agrocenosis conditions, the following may be named Cu, Ni, Zn, Fe and Mn. Thus, it allows expanding the priority list of usually identified trace elements for the purpose of agroecological monitoring from 4 (B, Zn, Mn, Cu) to 5-8 trace elements.

Table 3. The ranked sequences of the most intensively accumulated chemical elements (according to their ratio S_C/ S_g) in soil chronosequences in different bioclimatic conditions

No	Ranked sequences	S_C	S_g
	Steppe conditions		
S1	Sr>Na>Zn>Ca>Mg>Ni>Pb	17.4	23.4
S2	Cu>P>Ca>Zn>Ni>Fe>Pb>Mg	15.4	11.3
S3	Na>Sr>Ca>Zn>Pb>Mg>Fe>Co>Ni	16.9	18.9
S4	Sr>Zn>Na>Ca>Mg	18.1	17.6
	Forest-steppe conditions		
FS1	P>Zn>Cu>Pb>Ni>Ca>Mn>Fe	15.4	8.4
FS2	Sr>Na>Ca>P>Mg>Pb>Zn>Ni	18.9	16.2
FS3	Sr>Mg>Ca>P>Na>Zn	19.4	15.9

Due to the identification of the chemical elements with the maximum accumulation in clay in comparison with the soil using the value E_a distribution graphs (Fig. 1), it became possible to form ranked sequences of accumulation of elements (by the ratio S_c/S_g) (Table 3).

Different-aged soils (Table 3) are characterized by a more significant accumulation of a certain association of chemical elements in clay than in soil (E_a) which can be represented in the form of the following decreasing sequence: (Ca, Zn)>Mg>(Sr, Na, Pb)>(P, Ni)>Fe>Cu>Mn.



The proportion of soils of different degrees of erosion was (by 1984) 53.6% of the total area of soils of the Belgorod region (2713 thousand hectares). But due to the expansion of the process of erosion, during 30 years the total proportion of eroded soils is estimated to be about 60%. Water erosion of soils is a selective process which results in the selection of particles with a lower density of the solid phase and more enriched with organic matter, so, the particles most actively involved in the transport of sediments are particles with the hydraulic size of <0.01 mm. The grain size distribution of the products of the solid runoff is definitely heavier than the original soil which is associated with a decrease in its content of large dust fraction (0.05-0.01 mm) and an increase in the amount of silt fraction (<0.001 mm) (Tanasienko *etal.*, 2011).

Therefore, the elements in the above association which accumulate in the clay fraction will be most intensively lost in case of an active erosion of soil on a plowland. This, along with the biological removal, will determine their deficiency which requires regular monitoring and compensation of the deficit with microfertilizers. Analysis of the ranked sequences of the accumulation of elements in clay in comparison with the total soil content (Table 3 and Fig. 1) shows that as the duration of pedogenesis increases, the concentration P, Cu, Ni in clay decreases in conditions of steppe soil formation and the concentration Cu, Fe, Mn in clay decreases nthe forest-steppe conditions.

Soils of the same age in the conditions of the steppe and forest-steppe differ in the intensity of the accumulation of elements in the clay: in the steppe conditions, they accumulate more actively Cu, Ni, Fe, Pb and in forest-steppe conditions more Sr and Na. Regardless of the bioclimatic differences in clay as compared with the total content, the most intensive accumulation occurs P, Ca, Mg, Zn.

The trace elements content which is biogenic in nature, depends little on the time of pedogenesis. However, if the sum of such elements of biogenic accumulation Si, Al, K and Ca (through S_c/Sg) is expressed as their regular accumulation in the clay fraction as the time of pedogenesis increases, it is found.

CONCLUSION

To identify a possible trace elements deficiency and eliminate it, it is necessary to organize soil-ecological monitoring with the inclusion of elements into the controlled indicators that affect the growth and development of plants, their yield and the quality of the products.

The proposed method for estimating the biogeochemical transformation of forest-steppe soils of the Chernozem series by 16 diagnostic macroelements and trace elements which are accumulated or carried away by soil solutions from the humus horizons, makes it possible to construct a ranked sequence of macroelements and trace elements according to the rate of their accumulation which is of practical importance for forecasting the opposite process the loss of trace elements as a result of their biological removal from the soils of agrolands capes. The agropedocenosis requires periodic diagnostics of the trace elements deficiency and its correction by adding micro fertilisers to compensate for the loss of the most deficient trace elements: Cu, Ni, Zn, Fe, Mn as well as Mo, I, B.

In the conditions of erosive agrolandscapes of the forest-steppe and steppe with soils of loamy composition, due to the selective removal of particles by water erosion, the following major deficiencies can be expected in the following chemical elements useful for plants: Ca, Zn, Mg, Ni, P, Mn (in order of decreasing importance). Thus, in conditions of slope farming, control over their content becomes a priority activity in the management of the biogeochemical situation in the arable layer and in the rhizosphere zone.

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