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Results migration mobility investigation of microelements in the soil horizons under the influence of humus and carboxylic acids

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Formation of regular soil profiles podzols of boreal zone is defined by extracting features of humic and carboxylic acids formed during the biodegradation of plant litter. The structure features of soil profiles associated with variable, but high rates of downward filtering of these aggressive acids in landscapes with seasonal humidity. We experimentally simulated these conditions for studying a wide range of mobility of trace elements in soil horizons [*Alekhin and Kostyukova*, 2002].

Experimental methodsreceptions at carrying out of these experiences were similar to what are used at chromatographic differentiation into columns with processing of results by a method of concentration curves [*Alekhin and Lakshtanov*, 2008; *Lakshtanov and Alekhin*, 2005].

Objects and methods.

Soil and soil water samples were collected in Meshcherskaya lowland. Soil water was filtered through the filter with pore dimension of 0.2 micron.

Four horizons of podzolic soil (humus (A), eluvial (E), illuvial ferruginous (Bf) and gley horizon transition from illuvial to the parent rock (BCg)) were used in experiment.

Four columns which were tightly closed have been made of the selected material.

At the first stage of the experiment through each column the distilled water was passed for research of migration of trace elements at its infiltration as analog of fresh meteoric precipitation through soil. Then through columns the distilled water with addition sodium azide (for suppression of ability to live of microorganisms of soils) was passed.

The second stage of the experiment consisted in filtering through columns of the solution close on properties soil, with initially high content of humic and fulvic acids (with the addition of sodium azide).

At the third stage in this solution, related soil, carboxylic acids: acetic, lemon and oxalic in a ratio 1: 0,05: 0,003 were added. Such concentration ratio of acids was chosen because it close to a natural ratio in water extracts from soils and acidity (pH = 4,2) the solution is comparable to natural size [Hees et.al., 1996]. Addition of these acids in filtrant allowed to make active process of migration of elements of soil layers, remaining within the limits of experiment approach to natural process.

At the fourth stage of the experiment polyelement standard ICP-MS-68B Solution A (High-Purity Standards) was added to a solution with humic and carboxylic acids. The standard solution contains elements (Al, As, Ba, Be, Bi, B, Cd, Ca, Ce, Cs, Cr, Co, Cu, Dy, Er, Eu, Gd, Ga, Ho, In, Fe, La, Pb, Li, Lu, Mg, Mn, Nd, Ni, P, K, Pr, Re, Rb, Sm, Sc, Se, Na, Sr, Tb, Tl, Th, Tm, U, V, Yb, Y, Zn) with concentration 100,0 ± 0,5 mg/l. The standard was dissolved so that initial concentrations of all elements in a solution were 1 mg/l (pH = 3,5).

Addition of microelements given the chance to study method of adsorption curves of elements by columnar material (soil), and also to compare concentration of trace elements in filtrates.

Filtrates were selected time a day during all experiment. In parallel with sampling potentiometry (pH, pNa, pCa) for control of change of indicators were spent. Each following stage began after an establishment in system of stable indicators. The mass spectrometer of the high permission with is inductive-connected plasma ELEMENT of 2 Thermo Finnigan was applied to definition of concentration of trace elements in filtrates.

Results of research of a desorption of elements at various modes of filtering. Activity of a desorption of trace elements was defined by the coefficient of delay calculated on the equation: $R_1 = 1 - C_{filtrate} / C_{initial\ solution}$, where $C_{filtrate}$ is concentration of element in the filtrate, $C_{initial\ solution}$ is concentration of element in filtrante (initial solution).

For the first column (humus horizon) rows of microcells on increase in migratory activity have the following sequences: at a filtration of the distilled water: Eu< Er< Dy< Sm< Gd< Pr< Cd< La< Nd< Ce< Pb< Ti< Cu< Sr< Ba< Zn< Fe< K. At a filtration of natural solutions (soil water): Sr (0,94)< Ba (0,27)< Eu (-5,32)< Ti (-5,66)< Cd (-6,72)< Er (- 8,15)< Dy (-11,71)< Gd (-18,37)< Nd (-29,51)< Pb (-37,59)< La (-40,33)< Pr (-41, 13)< Ce (-59,98)< Sm (-69,75)< Fe (-107,40)< Cu (-244,08)< K (-1,8 * 104)< Zn (-2, 7 * 1012). At a filtration of natural solutions with carboxylic acids: Sr (-0,2)< Ba (-1,22)< Cd (-10,31)< Eu (-12,54)< Ti (-26,21)< Er (-36,06)< La (-37,94)< Nd (-41,36)< Gd (-46,10)< Pr (-49,09)< Dy (-49,23)< Sm (-53 , 37)< Ce (-55,83)< Cu (-255,66)< Pb (-258,51)< Fe (-656,10)< Zn (-4 * 104)< K (-3 * 107). Addition carboxylic acids increases the transfer of trace elements (except Zn), but mobility rows essentially don't differ from rows transport by fulvic acid drainage water.

The material of the second column (eluvial horizon) differs from the first considerably the smaller maintenance of humus, therefore rows of migratory mobility slightly different, but all basic laws remain the same: at a filtration of the distilled water: Eu< Er< Dy< Gd< Sm< Pr< La< Nd< Cd< Ce< Pb< Ti< Cu< Sr< Ba< K< Fe< Zn. At a filtration of natural solutions: Sr (0.37)< Ba (-0.58)< Ti (-2.10)< Er (-3.29) < Dy (-4.31)< Eu (-4.46)< Gd (-6.36)< Cd (-9.3)< Nd (-11.47)< Pr (-14.10)< Pb (-16.7)< La (-16.85)< Sm (-22.23), Ce (-22.23)< Fe (-42.51)< Cu (-5683.58)< K (-18279.29)< Zn (-9.9 * 1011). At a filtration of natural solutions with carboxylic acids: Sr (-0.15)< Ba (-0.68)< Cd (-3.49)< Er (-3.76)< Eu (-3.96)< Dy (-9.18)< Gd (-14.69)< Ti (-15,28)< Nd (-18.30)< Sm (-18,44)< Pr (-27,34)< La (-29,17)< Ce (-37,34) < Cu (- 104,25)< Pb (-109,93)< Fe (-186,93)< Zn (-52242,14)< K (-4.1 * 106).

For the third column following numbers of migratory mobility were received: at a filtration of the distilled water: Pr< La< Ce< Nd< Sm< Gd< Eu< Dy< Er< Ti< Cd< Pb< Sr< Ba< Cu< Fe< K< Zn. At a filtration of natural solutions: Sr (-0,02)< Er (-1,37)< Ti (-1,91)< Ba (-2,30)< Nd (-9,45)< La (-10, 27)< Fe (-10,45)< Ce (-11,39)< Pr (-15,44)< Gd (-58,16)< Eu (-81,62)< Cd (-91,12)< Pb (-96,28)< Dy (-131,96)< Sm (-162,03)< Cu (-1195,10)< K (-15249,37)< Zn (-4,3 * 1011). Comparing with the previous columns, it is possible to notice that values of coefficients of delay Gd, Eu, Cd, Dy and Sm have decreased that shows increase in their migratory mobility. Reduction of their migratory activity is visible on values of coefficients of delay Cu and Fe. The coefficient of delay Sr became negative, it shouldn't be adsorbed. At a filtration of natural solutions with carboxylic acids: Sr (-0,47)< Ba (-4,25)< Ti (-32,21)< Ce (-1443,22)< Nd (-1694,37)< Cd (-1768,45)< La (-1988,63)< Fe (-2014,10)< Cu (-2201,85)< Pb (-3633,88)< Dy (-6688,51)< Gd (- 7080,42)< Eu (-7567,98)< Er (-7709,76)< Pr (-8005,51)< Sm (-8791,10) < Zn (-151862,87)< K (-6, 5 * 107). In comparison with the previous regime the sequence changed in copper position and if to compare to other columns, - that it is necessary to note cardinal change in the ratio of the coefficients of delay in group of the rare earth elements. But the main difference from other columns and the previous regimes is considerable changes of coefficients of delay for the majority of elements. It speaks about intensification of carrying out of elements at addition carboxylic acids for illuvial horizon of podsolic soils.

For the fourth column at a filtration of the distilled water the received row of migratory activity looks as follows: Sr< Cd< Ba< La< Ce< Pr< Nd< Sm< Eu< Gd< Dy< Er< Pb< Ti< Fe< Cu< Zn< K. At a filtration of natural solutions: Sr (-0,02)< Ba (-0,54)< Ti (-0,57)< Cd (-6,66)< Fe (-6,84)< Nd (-10,67)< Pb (-15,05)< Eu (-16,87)< La (-18,33)< Gd (-23,24)< Dy (-25,01)< Ce (-25,95)< Pr (-46,30)< Er (-50,97) < Sm (-81,10)< Cu (-4824,24)< K (-8139,56)< Zn (-3.5 * 1012), for this column it differs from previous in high coefficient of delay of iron. At a filtration of natural waters with addition of carboxylic acids iron moving by the end of row of migratory mobility after all number of the rare earth elements also is marked: Sr (-0,20)< Ba (-0,99)< Cd (-6,74)< Ti (-23,44)< Eu (-58,740)< Er (-74,77)< Fe (-136,89)< Dy (-161,01)< Gd (-248,92)< Nd (-308,45)< Sm (-335,53)< La (-338,43)< Pr (-409,48)< Pb (-410,30)< Ce (-545,80)< Cu (-1564,75)< Zn (-149511,07)< K (-4.4 * 107).

Results of experiments show that actively migration of trace elements occurred in illuvial horizon that is natural as trace elements contain in it in the greatest quantity. If to compare various regimes for the majority of considered trace elements (excepting iron, potassium, zinc) the adsorptions occurred most actively in the infiltration of the soil solution with carboxylic acids.

Results of research of elements adsorption. The characteristic of intensity of realization of process of adsorption is the indicator of integrated coefficient of delay:

$R_2 = 1 - (\sum(C_{filtrate} * V_{filtrate})/(C_{initial\ solution} * \sum V_{filtrate}))$, where $C_{filtrate}$ is concentration of element in the filtrate, $V_{filtrate}$ is the volume of filtrate taken, $C_{initial\ solution}$ is concentration of element in filtrante (initial solution). The integral coefficient of delay are presented in Tables 1 and 2.

Table 1. Integrated factors of a delay of elements

Soil horizon	Cd	Sr	Ba	Pb	Cu	Fe	Zn	K
A	0,7	0,9	0,9	1	1	-17,5	-1,6	-0,1
E	0,3	0,4	0,4	0,7	0,5	-2,9	-0,8	-0,04
Bf	0,2	0,3	0,3	0,7	0,5	-7,1	-3,7	-0,05
BCg	0,2	0,2	0,2	0,5	0,3	-0,6	-1,4	0

Table 2. Integrated factors of a delay of elements

Soil horizon	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Er
A	1	1	1	1	1	1	1	1	1
E	0,8	0,6	0,5	0,4	0,4	0,4	0,4	0,4	0,4
Bf	0,7	0,5	0,4	0,4	0,3	0,3	0,4	0,3	0,2
BCg	0,8	0,7	0,6	0,6	0,5	0,5	0,6	0,5	0,4

On the calculated integrated coefficients of delay it is visible that all considered elements most actively sorbed in humus horizon (especially rare earth elements).

Adsorption of bivalent metals (Cu, Sr, Cd, Pb, Ba) is shown more poorly in BCg horizon (table 1 and fig. 1-3); adsorption of rare-earth elements is shown in the minimum degree in illuvial and eluvial horizons (table 2 and fig. 4,5).

As a result of an ionic exchange and extraction from soils, against adsorption of most trace elements, the desorption for Fe, Zn and K (table 1 and fig. 6) continues.

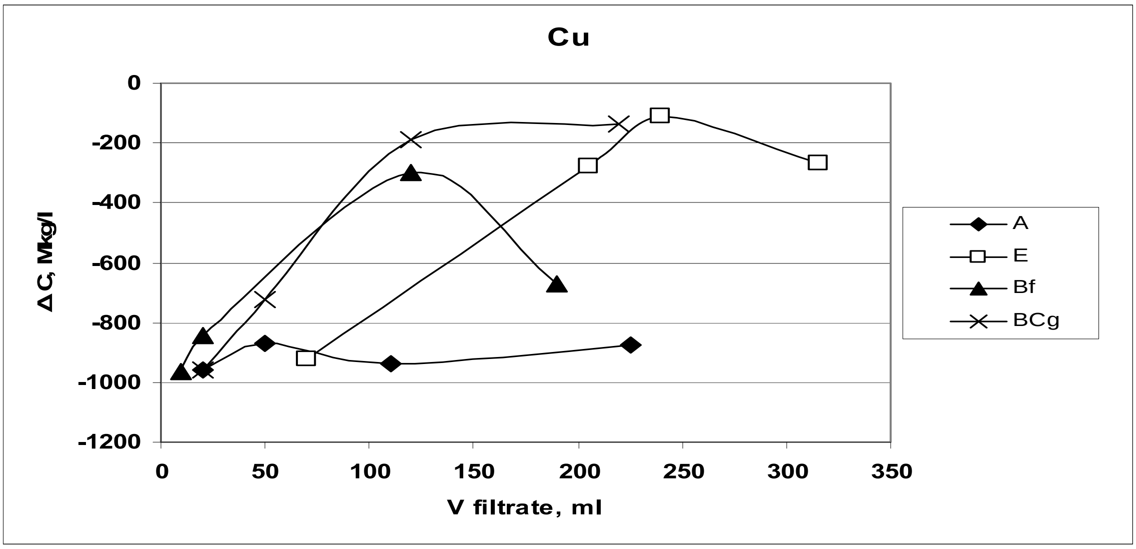

Fig. 1. Adsorption-desorption curves of Cu

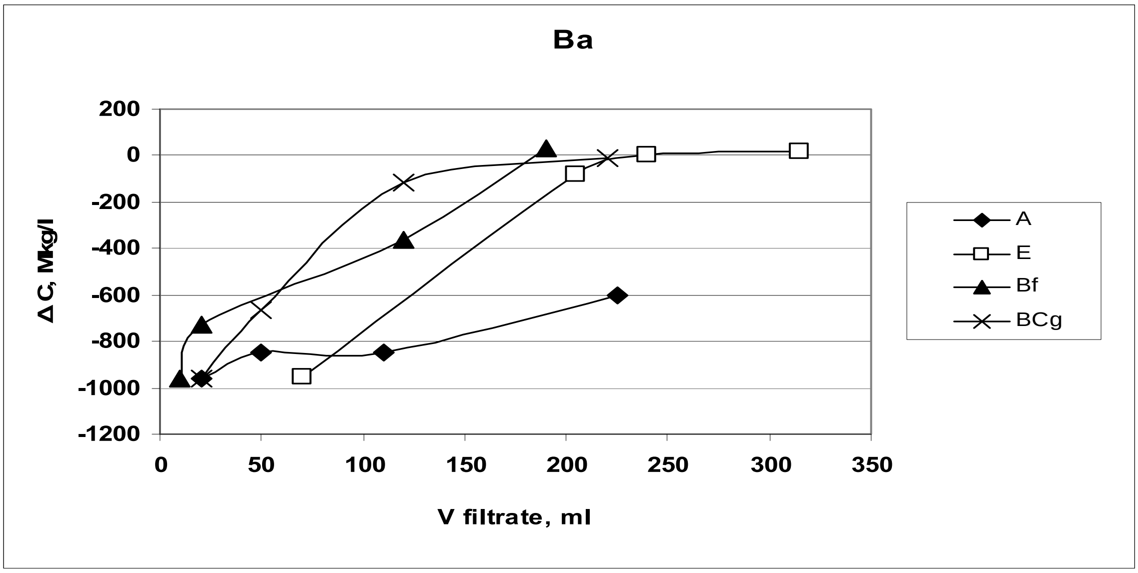

Fig 2. Adsorption-desorption curves of Ba

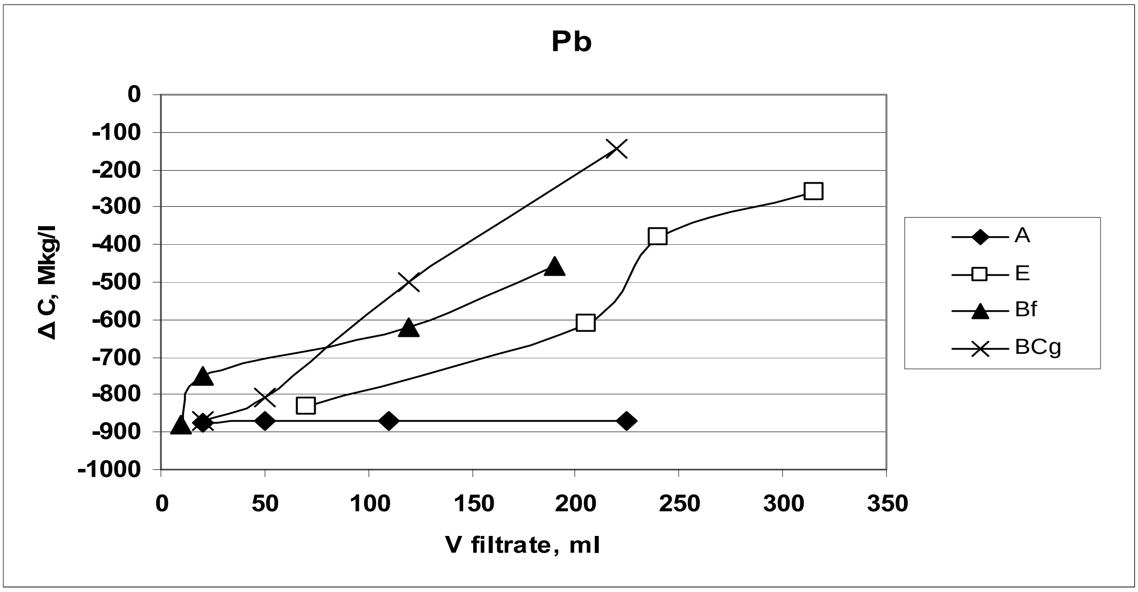

Fig 3. Adsorption-desorption curves of Pb

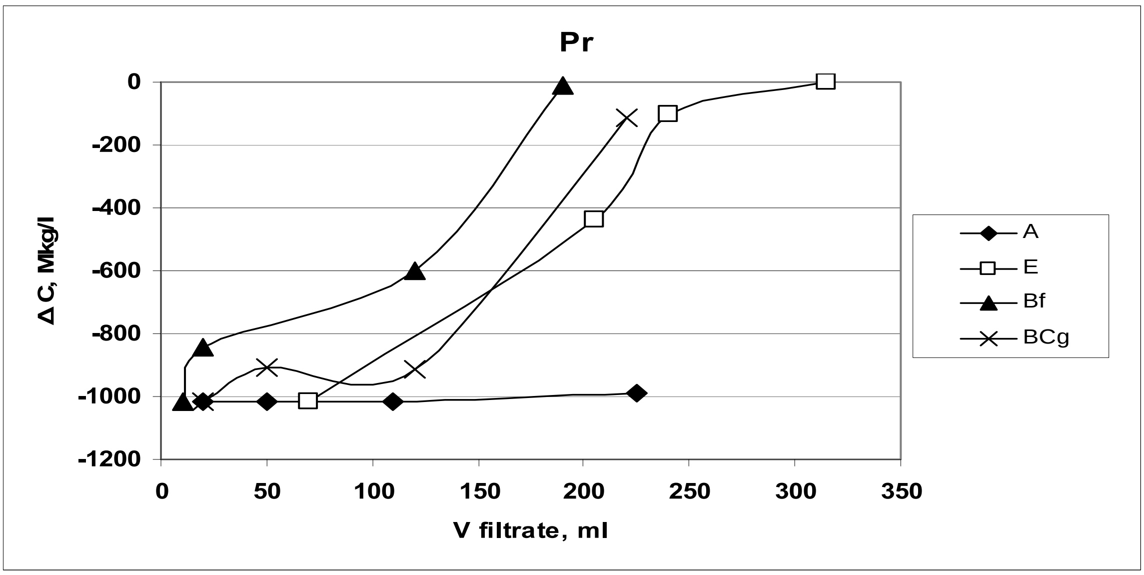

Fig 4. Adsorption-desorption curves of Pr

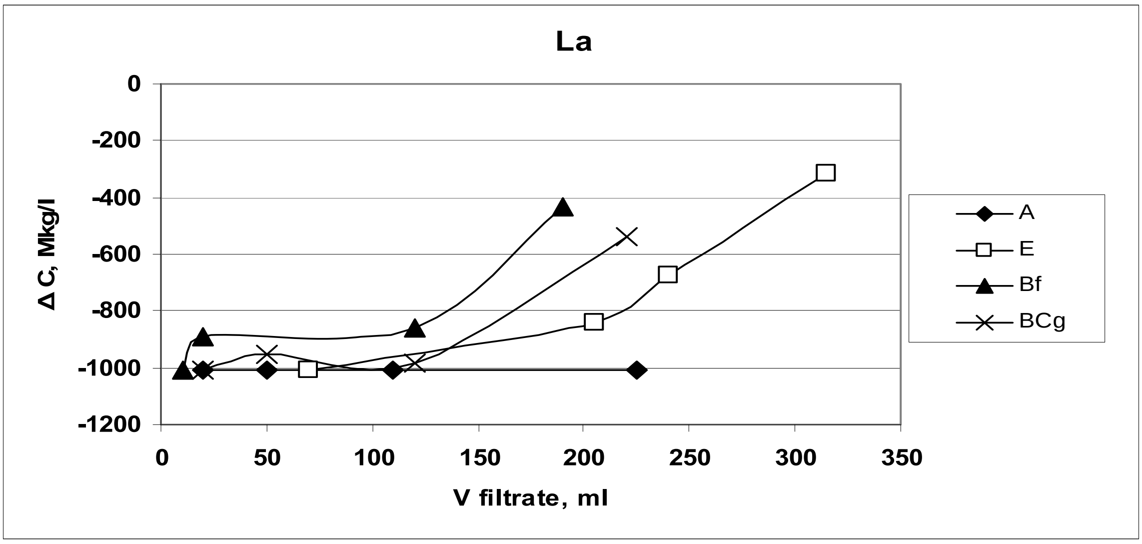

Fig 5. Adsorption-desorption curves of La

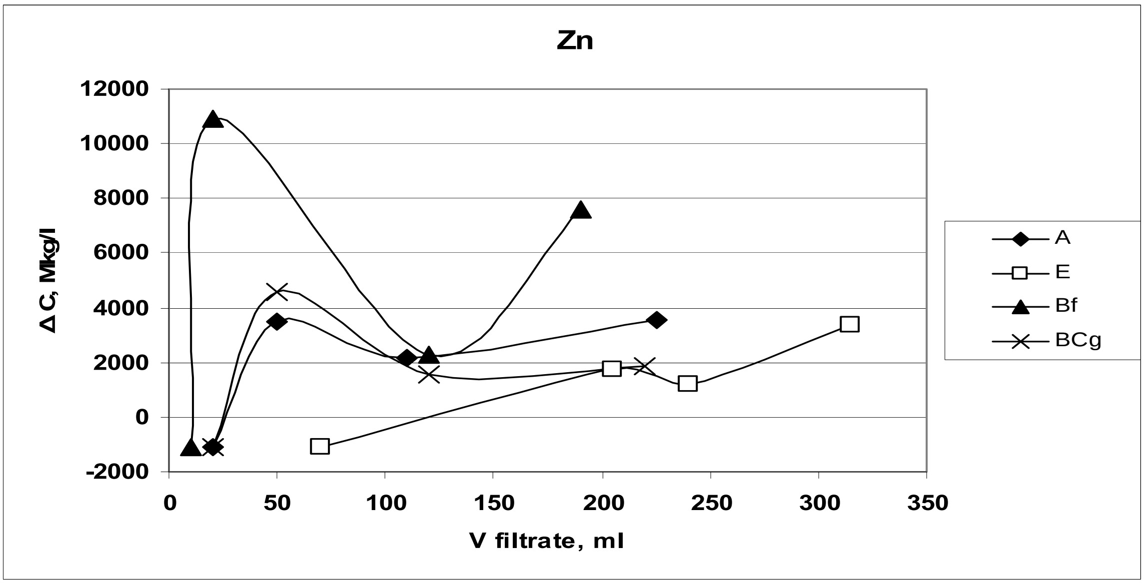

Fig 6. Adsorption-desorption curves of Zn

Grants of RFFR 11-05-00464-a, 11-05-00638-a

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