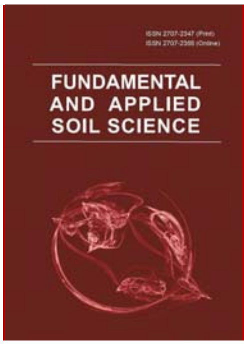

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Indicators for pedogeochemical barriers of heavy metals' migration

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The aims of this study were to substantiate indicators for pedogeochemical barriers of heavy metals's migration. The concept of pedogeochemical barriers of heavy metals'migration. Pedogeochemical migration barrier is part of the soil horizon or soil profile, where, as a result of special pedosubstantsiya availability and certain pedogeochemical reactions percolation, there is a significant accumulation of some chemical elements. These barriers act as a «substation-reactionary phenomenon». Pedogeochemical migration barrier grouped into five types: mechanical A, physical (sorption) B, physicochemical (ion exchange) C, chemical D and biological E. Indicators of geochemical migration barriers. To assess the geochemical barriers to migration, A. I. Perelman suggested using barrier contrast indicators and the barrier gradient. Wherein, the barrier contrast is calculated as the ratio of the chemical element concentration on the barrier to its quantity up to the barrier. Barrier gradient is the ratio of soil differences before and after the barrier to its length. Indicators of pedogeochemical migration barriers. In soil science, as the analogue of the barrier contrast are: the contrast ratio, the coefficient of intra-profile differentiation, alluvial-accumulative coefficients. As an analogue of the gradient barriers, there are indices of absolute and relative gradients of pedogeochemical migration barriers. Indicators of Pedogeochemical migration barriers manifest that in the chernozems of ordinary and southern at Kryvyi Rih areas, the accumulation of heavy metals in the humus transition and humus accumulation horizons has been revealed. Wherein, the more intensive action of soil migration barriers is naturally revealed in chernozems of ordinary, in comparison with chernozems southern.

Keywords: pedogeochemical migration barriers; substation-reaction phenomenon; heavy metals; soil; Krivorizhzhya

Introduction

The consensus between Humans and Nature can be achieved only by conserving and by protecting the soil as an irreplaceable component of the biosphere, its «biogeochemical membrane» and its «geochemical reactor» (Aparin, Aparin, 2012; Dobrovolskiy, 1997; Dobrovolskiy, Nykytyn, 2000). That is why the creative search for new ideas and the development of innovative technologies on their basis are so important. These technologies must mobilize the regenerative properties of the soi when it is contaminated with various chemical elements, including a heavy metals (HM) (Bradl, 2005; Dabahov et all, 2005; Kopcik, 2014; Vasilev, Chaschin, 2011).

In this regard, it should be noted that Alexander Perelman's concept of geochemical barriers to elemental migration (GChB) is a major scientific achievement in the second half of the twentieth century (Perelman, 1961). Time and practice have confirmed its importance for solving the most urgent problems in geochemistry and in environmental protection. This concept was very important for: chemical composition of rocks forecasting, contaminated land reclamation, as well as the spread of xenobiotics in the biosphere prevent preventing (Alekseenko, 2003; Chertko, 2008; Kuzmin, 2000; Maksimovich, Hayrulina, 2011; Maximovich, Khayrulina, 2014).

However, attempts to implement the concept of geochemical barriers to elemental migration in soil science were ineffective. The main reasons for this result were: (i) a domination of mechanical transfer for ideas of this concept, (ii) lack of features proper understanding for the soil unique structural and functional organization.

Recently, we began to develop an analogue for the concept of geochemical barriers elemental migration. Our new concept is maximally adapted for soil science and is called the doctrine of pedogeochemical barriers to elemental migration (PGChB). By the present time, we already analyzed the genesis'idea and definition of pedogeochemical barriers to heavy metals migration (Savosko, 2017), as well as the classification of pedogeochemical barriers to heavy metals migration (Savosko, 2018).

The main objective of this work was to give scientific credence to indicators for pedogeochemical barriers to heavy metals migration.

Materials and methods

Materials of research are the scientific publications about regularities of heavy metals inpute, distribution and content of TM in soils.

Methods of research are analysis and synthesis, induction and deduction, analogy and formalization, abstraction and concretization, classification and modeling.

Results and discussion

Definition of pedogeochemical barriers to elemental migration. In our understanding, the pedogeochemical barrier to element migration is a part of the soil horizon or soil profile, where, as a result of the presence of special pedosubstantions and the occurrence of special pedogeochemical reactions, significant accumulation of individual chemical elements occurs (Savosko, 2017; Savosko, 2018). It is also important to note that PGhB migration is manifested as a «subjective-reactionary phenomenon», i.e. the in-ground migration flows chemical elements due to interaction with the components of the soil solid phase are concentrated on strictly deterministic the soil profile parts (Fig. 1).

Explain the basic essence of PGHB on the example of HM distribution patterns. As is well known, in soils the metals are present in solid, liquid, gaseous and alive all its phases (Motuzova, 2009; Savosko, 2016; Sposito, 2008; Tan, 1982).

However, the liquid and solid soil phases form the basis of all soil chemical elements pedogeochemistry. In this case, the solid soil phase is a «pedogeochemical matrix», which contains the main amount of chemical elements. At that time, as the liquid soil phase is the «pedogeochemical field», where the most movable and most reactionary-capable forms («portions») of chemical elements are concentrated. In general, the interaction between the solid and liquid soil phases forms a dynamic equilibrium of the whole pedogeochemical system. The components of the solid soil phase, as well as the reaction of its substances with the metals of the liquid soil phase and predetermine the effect of pedogeochemical barriers to elements migration (Fig. 1).

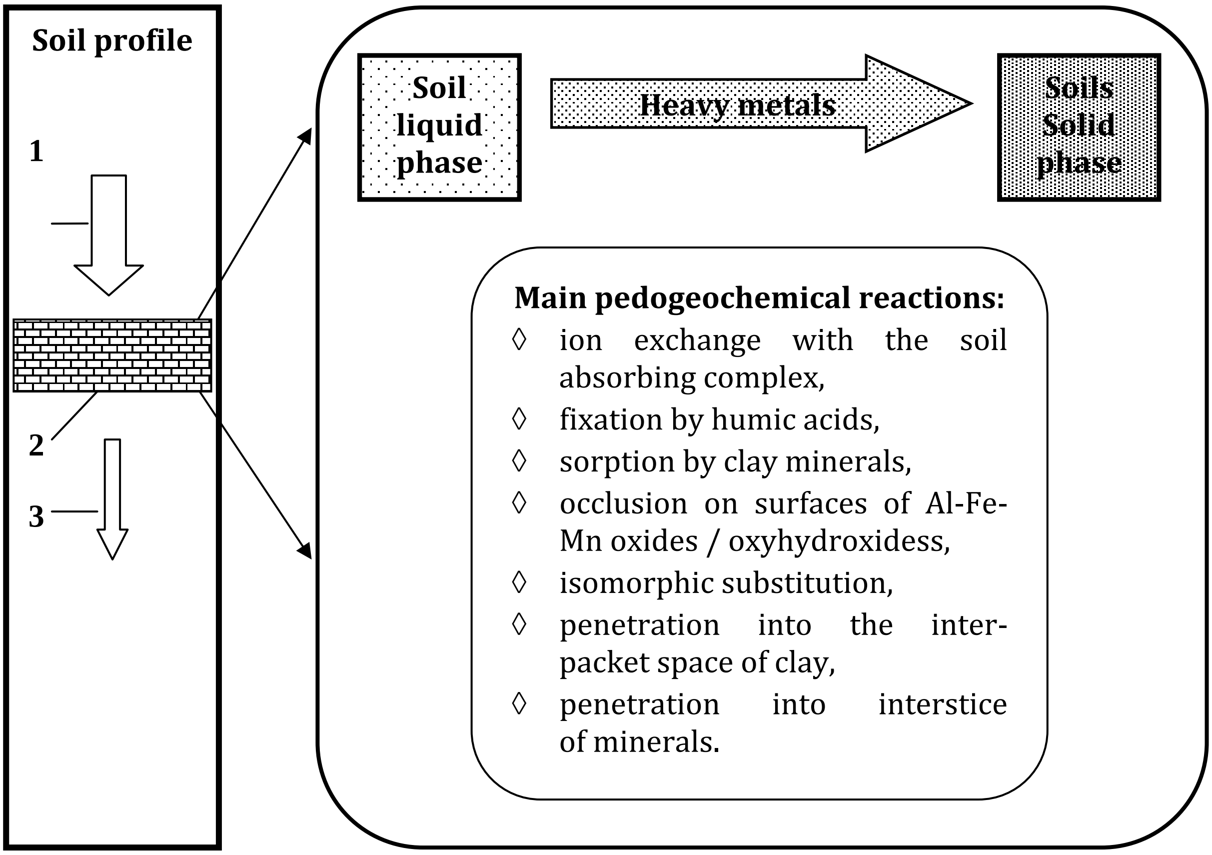

Fig. 1. The main components and the action principles of the pedogeochemical barrier to element of migration (by V. M. Savosko (Savosko, 2017) with our refinements and additions)
Trend of heavy metals migration: 1 – before the barrier; 2 – after the barrier; 3 – area of metal concentration on the barrier.

We believe that pedogeochemical barriers to elements migration are expediently grouped into five types. These types correspond to kinds of the soil absorption capacity by K.K. Gedroits (Gedroyts, 1955). In general, we emphasize the following pedogeochemical barriers types: mechanical A, physical (sorption) B, physico-chemical (ion exchange) C, chemical D and biological E. It should also be noted that within these types we additionally allocated classes and subclasses of the pedogeochemical barriers to element migration. In this regard, the effects and mechanisms of action, agents-absorbers, as well as special reactions of pedogeochemical interaction were taken into account (Savosko, 2018).

Geochemical barriers to elemental migration Indexes. A. I. Perelman suggested using barrier contrast indexe and barrier gradient indexe to evaluate the geochemical barriers (Perelman, 1961, 1972, 1989). In this case, the barrier contrast indexe is calculated as the ratio of the chemical element concentration at the barrier to its amount befor the barrier. While the barrier gradient indexes are a characteristic of its geochemical conditions. Since it represents the ratio of the geochemical parameters difference (pH, oxidation-reducing potential, etc.) before and after the barrier to its length.

Calculation method for pedogeochemical barriers to elemental migration Indexes. We believe that in the soil science, the Contrast Index (Icn), Intra-Soil Profile Differentiation Index (Ispd), Eluvial-Accumulative Index (Iea) can be analogous to the geochemical barriers to elemental migration Indexes. It is expedient to carry out their calculation according to formulas 1–5.

$$Icn = \frac{C(i)}{C(0)} \quad (1)$$

$$\text{Cvwa} = \frac{\sum_{i=1}^{n}(C(i) * h(i))}{\text{H}} \quad (2)$$

$$Ivwa\_cn = \frac{Cvwa}{C(0)} \quad (3)$$

$$\text{Ispd} = (Icn - Ivwa\_cn) * h(\text{i}) \quad (4)$$

$$Iea = (\frac{C(\text{i}) * \text{R}(0)}{C(0) * R(i)} - 1) * 100 \quad (5)$$

Where: *Icn – Contrast Index*; C(i) – metal content in i soil horizon, mg/kg; C(0) – metal content in parent rock, mg/kg; Cvwa – volume-weighted average metal content in soil profile, mg/kg; h(i) – i soil horizon depth, cm; H – soil profile depth, cm; Ivwa_cn – volume-weighted average concentration index; *Ispd – Intra-Soil Profile Differentiation Index*; *Iea – Eluvial-Accumulative Index;* R(0) – stable component content («witness») in parent stock, %; R(i) – stable component content («witness») in I soil horizon, %.

The philosophy used to justify the pedogeochemical barriers to elemental migration indexes was based on the following prerequisites. First, the scientific forerunner of our methodology were scholarly writings of soil science classics: P. P. Kossovich (1916), A. A. Rode (1937), as well as their talented followers: M. A. Glazovskaya (1988), E. G. Nechaeva (1985), G. A. Simonov (2004). These scientific works were theoretically substantiated and practically repeatedly verified. Secondly, the soil horizon and soil profile are the main structural and functional units pedogeochemical barriers to elemental migration. Third, the conditional «zero point» were used: (i) metal content in parent rock for Contrast Index and for Eluvial-Accumulative Index; (ii) volume-weighted average metal content in soil profile for Intra-Soil Profile Differentiation Index.

Pedogeochemical barriers to elemental migration Indexes application allows you to make clear and unambiguous conclusions. So, if the value of Contrast Index is greater than one (Icn > 1), then in a certain area of the soil profile the accumulation of a chemical element occurs. But, if the Contrast Index value is less than one (Icn < 1), then the leaching of the chemical element occurs. The positive values of the Intra-Soil Profile Differentiation Index (Ispd > 0), as well as the Eluvial-Accumulative Index (Iea > 0), manifest the chemical element accumulation in a certain area of the soil profile. Negative values of the Intra-Soil Profile Differentiation Index (Ispd < 0) and the Eluvial-Accumulative Index (Iea < 0) manifest the chemical element leaching in a certain area of the soil profile.Modules of these pedogeochemical Indixes demonstrate the intensity of chemical element leaching or the intensity of chemical element accumulation.

As we believe in soil science, the values of Absolute Gradient Index (AGI) and Relative Gradient Index (RGI) are expedient to be used as analogues of geochemical barrier gradient indexe. These indices should be calculated according to formulas 6–7.

$$AGI = \frac{Me(i) - \text{Me}(\hat{\text{i}})}{\text{h(i)}} \quad (6)$$

$$RGI = \frac{Me(i) - \text{Me}(\hat{\text{i}})}{\text{Me}(\hat{\text{i}})} * 100\% * \frac{1}{\text{h(i)}} \quad (7)$$

Where: *AGI – Absolute Gradient Index*; *RGI – Relative Gradient Index*; *Me(i)* – metal content in i soil horizon; *Me(o)* – metal content in parent rock; *h(i)* – soil horizon depth, cm.

The values of the Absolute Gradient Index and Relative Gradient Index allow doing the following conclusions about the pedogeochemical situation in the soil profil. Thus, the positive values of these gradients the accumulation of chemical elements in a certain horizon of the soil profile manifest. While the negative values of these gradients, the leaching of chemical elements in a specific soil profile horizon demonstrate. Moreover, the modules of these gradients the intensity of the corresponding pedogeochemical processes indicate. It should also be noted that Absolute Gradient Index of pedogeochemical barriers to elemental migration is «vertically oriented». This allows estimating the distribution of only one chemical element within the soil profile. While the Relative Gradient Index of pedogeochemical barriers to elemental migration can be used to analyze the distribution of: (i) one chemical element throughout the soil profile («vertical analysis»), (ii) several chemical elements in one soil horizon («horizontal analysis»).

Pedogeochemical barriers Indexes in soil profile at Kryvyi Rih area. In Kryvyi Rih Ore-Mining basine the major type of soil formation is chernozem, which characterized by intense accumulation of humus (human type), neutral reaction and calcium predominance in the soil absorbing complex (Dolina & Smetana, 2014; Fridland, 1981; Savosko, 2015; Vernander et al., 1986). These soils are classified as *Chernozems* by International Soil Classification Systems (SCS) (World reference base for soil resources, 2014), *Chernozems Ordinary* and *Chernozems Southern* by Ukrainian SCS (Polupan et al., 2005) and *Mollisols* by USA SCS (Soil Survey Staff, 2014).

Chernozems Ordinary is commonly found on the watershed plateau, rolling interfluvial plain and high terraces in the central and northern parts at the Kryvyi Rih area. These soils are characterized by: a medium-depth humus horizons (50–60 cm), a average humus content (4,5–4,7%), a soil solution neutral reaction (pH_{H20} 7,1–7,2), a goode developed soil absorbing complex (cation exchange capacity – 35–40 milliequivalents /100 g of dry soil). The *Chernozems Ordinary* soil profile is characterized by three soil horizons designated as: a humus surface horizon (Ah 0–30 cm), an elluvial subsoil horizon (Bk 60–90 cm) and a weathered horizon (Ck from 120 cm) and two intermediate layers ABk (30–60 cm), BCk (90–110 cm).

As we have previously noted (Savosko, 2009), among heavy metals, Fe has maximum concentrations in *Chernozems Ordinary* at local background area of Krivorozhya. This metal content (in mobile forms – digested in one normal nitric acid) varied from 670 to 1570 mg / kg of dry soil. The amount of Mn is 5–10 times smaller and amounts to 100–340 mg / kg of soil. The content of Zn and Ni is approximately equal to 15–45 mg / kg of soil, that, in comparison with Fe, two orders less. The amount of Cu and Pb are also at the same level 2–10 mg / kg of soil, which are three orders less than Fe. Minimum content detected for Cd (0.3–0.9 mg / kg of soil), which is four orders less than Fe.

Our methodology of soil sampling (every 10 cm) allows us to apply of Contrast Index values for HM distribution analysis in the separate layers of the *Chernozems Ordinary* soil profile at Kryvyi Rih local background area (Savosko, 2003; Savosko, 2009; Savosko, 2016). So, we can consider the manifestation of the pedogeochemical barriers to elemental migration in the soil profile of these *Chernozems* (Fig. 2).

Three groups of metals are distinguished, depending on the values of Contrast Index (Fig. 2). The first group (Fe Mn) is characterized by the maximum values of these indices (*Icn* = 1,2–2,7). In the top layer of soil (0–30 cm) the contents of these metals are approximately the same level. Nevertheless, Mn accumulation (*Icn* = 2,6–2,7) is somewhat higher than Fe accumulation (*Icn* = 1,7–2,2). The maximum accumulation of metals of this group was found in the middle layer in soil profile of the *Chernozems Ordinary* (30–60 cm): Fe – *Icn* = 2.0–2.2; Mn – *Icn* = 3.1–3.2. Then the concentrations of Fe and Mn gradually decrease with depth (70–120 cm) to parent rock values.

Zn, Ni, Cu were assigned to the second group of metals (Fig. 2). Their distribution is similar to the previous metals, but only in the main trend. Thus, the maximum Zn, Ni, Cu

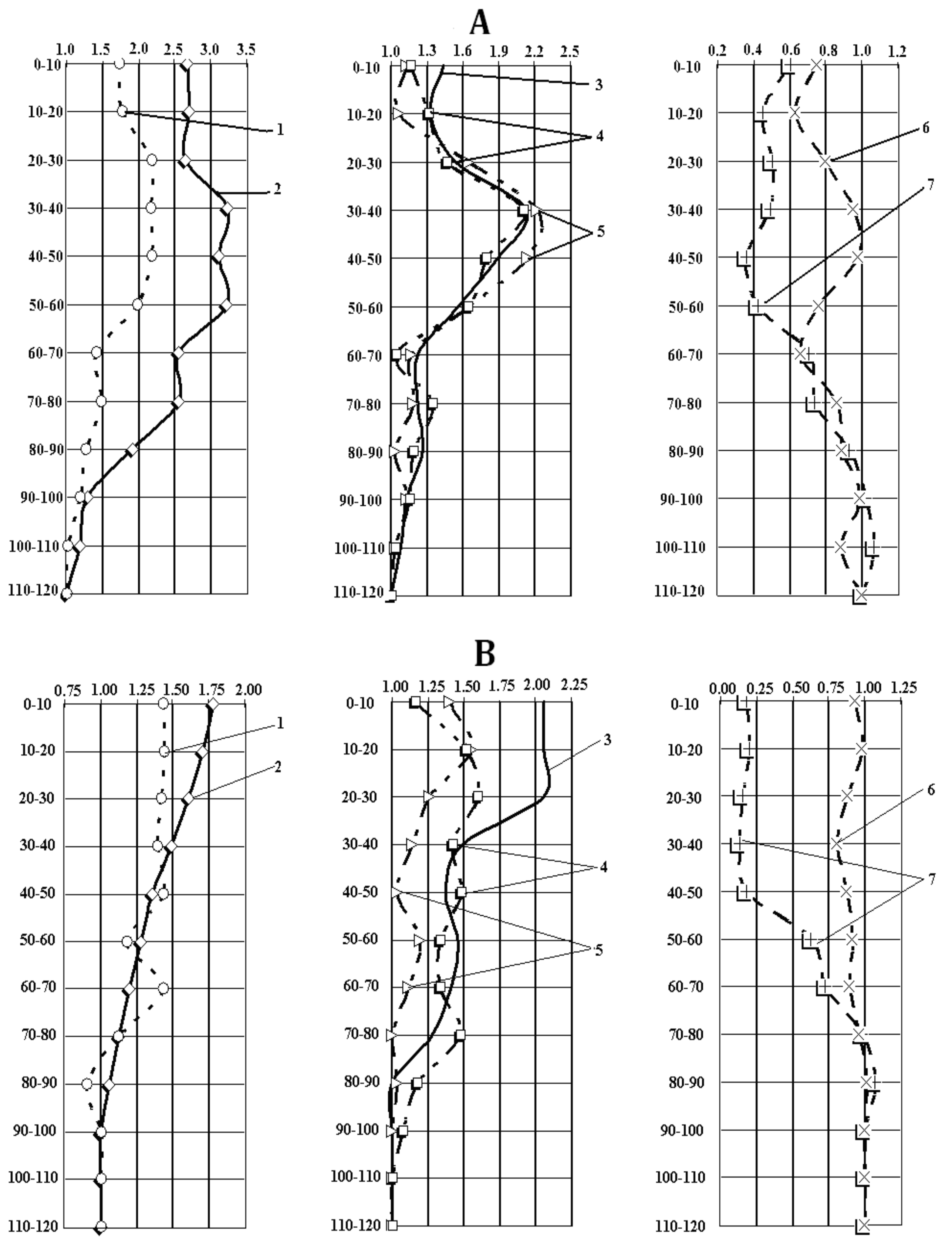

Fig. 2. Heavy Metals Contrast Index in Chernozems layers at Kryvyi Rih area
axis abscissa – Contrast Index; axis ordinate – depth, cm;
A – *Chernozems Ordinary*; Б – *Chernozems Southern*;
1 – Fe; 2 – Mn; 3 – Zn; 4 – Ni; 5 – Cu; 6 – Pb; 7 – Cd.

accumulation is in the upper (0–30 cm) and middle (30–60 cm) layers of the soil profile at *Chernozems Ordinary*. But it should also be noted low levels of their accumulation (*Icn* = 1,1–2,2), as well as their maximum content is in the 40–50 cm soil layer (*Icn* = 2,1–2,2).

Pb and Cd are assigned to the third group of metals (Fig. 1). Leaching of these metals is the main specialty their distribution in all soil profile of the *Chernozems Ordinary*. It should also be noted that the maximum leaching was revealed: for Pb in the soil layer 10–20 cm (*Icn* = 0,6); for Cd in the soil layer is 40–50 cm (*Icn* = 0,4).

The Intra-Soil Profile Differentiation Index (Ispd) calculated results indicate the occurrence of processes HMs accumulation and HMs leaching in the *Chernozem Ordinary* soil profile at Krivorozhie local background area (Table 1). Thus, in comparison with the weighted average metal content, accumulation was revealed: in the humus surface horizon (Ah) for Fe, Mn, Zn; in the first intermediate layer (ABk) for Fe, Mn, Zn, Ni, Cu, Pb; in the elluvial subsoil horizon (Bk) for Cd; in the second intermediate layer (BCk) for Cd, Pb.

It should also be noted that in comparison with the weighted average metal content, leaching was found: in the humus surface horizon horizon (Ah) for Ni, Cu, Pb, Cd; in the first intermediate layer (ABk) for Cd; elluvial subsoil horizon (Bk) for Fe, Mn, Zn, Ni, Cu, Pb; in the second intermediate layer (BCk) for Fe, Mn, Zn, Ni, Cu. It is established that the maximum levels of metal accumulation are in the humus intermediate layer (Ispd = 1,88–20,73).

The table 1 data showed that among metals, the most intense accumulation is for Mn (Ispd = 20,73) and Cu (Ispd = 18,13). But, the least accumulation is for Pb (Ispd = 1,88 – 2,09). It should also be noted that the Intra-Soil Profile Differentiation Index values indicate that the metals accumulation dominates in the top part of the soil profile (Ah and ABk horizons). While the metals leaching of prevails in the lower part of the soil profile (Bk and BCk horizons).

Table 1
Geochemical barriers to heavy metals migration Indexes in *Chernozems Ordinary* soil profile at Kryvyi Rih area

Soil horizons	Fe	Mn	Zn	Ni	Cu	Pb	Cd
Intra-Soil Profile Differentiation Index (Ispd)							
Ah	6,77	6,67	0,45	-2,26	-3,53	-3,14	-4,48
ABк	13,34	20,73	13,14	13,98	18,13	1,88	-7,34
Bк	-8,63	-2,02	-7,21	-5,82	-8,19	-0,82	4,09
BCк	-11,48	-25,38	-6,38	-5,90	-6,40	2,09	7,73
Eluvial-Accumulative Index (Iea)							
Ah	89,26	172,42	43,80	30,68	28,02	-27,33	-48,81
ABк	111,16	219,31	86,10	84,84	100,20	-10,61	-58,33
Bк	37,95	143,47	18,30	18,83	12,47	-19,61	-20,24
BCк	9,32	23,27	10,43	8,74	7,77	-6,43	4,76
Absolute Gradient Index (AGI), mg/kg*cm^{-1}							
Ah	21,50	6,08	0,22	0,22	0,05	-0,03	-0,014
ABк	26,79	7,13	0,44	0,61	0,16	-0,01	-0,016
Bк	9,14	5,06	0,09	0,14	0,02	-0,02	-0,006
BCк	3,38	1,23	0,08	0,09	0,02	-0,01	0,002
Relative Gradient Index (RGI), %*cm^{-1}							
Ah	2,98	5,75	1,46	1,02	0,93	-0,91	-1,63
ABк	3,71	6,74	2,87	2,83	3,34	-0,35	-1,94
Bк	0,09	0,05	0,00	0,00	0,00	0,00	0,00
BCк	0,47	1,16	0,52	0,44	0,39	-0,32	0,24

The Alluvial-Accumulative Index values analysis allowed combining all metals into two groups. Metals from these groups are characterized by diametrically opposite tendencies of their distribution in *Chernozem Ordinary* soil profile at Krivorozhie local background area (Table 1). Thus, metals from the first group (Fe, Mn, Zn, Ni, Cu) are characterized by accumulation in all genetic horizons of these soils (*Iea* > 0). While metals from the second group (Pb, Cd) are characterized by leaching in all soil profile (*Iea* < 0). In this case, the maximum metals accumulation was revealed in the humus intermediate horizon (*Iea* = 84,84–219,31) and humus surface horizon (*Iea* = 28,02–172,42). It should also be noted that among metals, the highest accumulation levels were found for Mn (*Iea* = 219,31), Fe (*Iea* =111,16) and Zn (*Iea* = 86,10).

Absolute Gradient Index values manifest that the soil barrier properties are most effect in the humus intermediate horizon (ABk) at Kryvyi Rih Chernozem Ordinary (Table 1). Moreover, in this horizon, the greatest barrier effect acts for Fe (*AGI* = 26,79 mg/kg*cm^{-1}) and for Mn (*AGI* = 7,13 mg/kg*cm^{-1}). In general, Absolute Gradient Index values suggest that barrier phenomena cause the accumulation of certain metals: Mn, Fe, Zn in Ah-horizon; Mn, Fe, Cu, Zn, Ni in ABk-horizon; Mn, Fe in Bk-horizon; Mn in BCk-horizon. Relative Gradient Index value analysis allows you to make similar conclusions (Table 1). All pedogeochemical barriers Index analysis suggests that by degree of predisposition to the soil absorption at Kryvyi Rih area *Chernozems Ordinary* metals form next incremental series: (Cd, Pb) << (Cu <Ni <Zn) << Fe << Mn.

Chernozems Southern is commonly found on the watershed plateau, rolling interfluvial plain and high terraces in the southern part at the Kryvyi Rih area (Dolina & Smetana, 2014; Fridland, 1981; Savosko, 2015; Vernander et all, 1986). These soils are characterized by: a little-depth humus horizons (25–35 cm), a low humus content (3,1–3,4%), a soil solution weakly alkaline reaction (pH_{H20} 7,5–7,6), a goode developed soil absorbing complex (cation exchange capacity – 30–35 milliequivalents /100 g of dry soil).

The *Chernozems Southern* soil profile is characterized by three soil horizons designated as: a humus surface horizon (Ahk 0–20 cm), an elluvial subsoil horizon (Bk 50–70 cm) and a weathered horizon (Ck from 90 cm) and two intermediate layers ABk (20–50 cm), BCk (70–90 cm).

Heavy metals contrast Index analysis found out of thire distribution patterns in *Chernozems Southern* at the Kryvyi Rih local background area (Fig. 2). Analysis shows that, in Kryvyi Rih area *Chernozems Ordinary* the Mn and Fe amount decreases gradually and smoothly from the soil surface (*Icn* = 1,25–1,35 for Fe; *Icn* = 1,55–1,75 for Mn) to the parent rock. At the same time, a slight «splash» of the Fe content (*Icn* = 1.50) is set at a 60–70 cm depth, which may be due to the local geochemical barriers to heavy metals migration action. The maximum Zn, Ni and Cu amount was also detected in the top soil layers (0–30 cm). In these layers, their concentrations were practically at the same level (*Icn* = 2,1–2,2 for Zn; *Icn* = 1,15–1,55 for Ni; *Icn* = 1,20–1,25 for Cu). In deep soil layers (30–100 cm) the amount of these metals gradually decreases to the level parent rock. A small «momentum» of the Cu amount was detected at a 70–80 cm depth (*Icn* = 1.5), which can also be considered as to the local geochemical barriers to heavy metals migration action. Compared to other metals, the Cd distribution in the soil profile layers was very unique. Thus, in the top soil layers (0–50 cm) this metal leaching (*Icn* = 0,25) was established. However, in deep layers soils (50–100 cm), the Cd concentration increases to the parent rock levels. It was found that the Pb content in the *Chernozem Southern* profile was not different from that parent rock (Fig. 2).

Table 2 indicated that there were HM accumulations and HM leachings in the *Chernozem Southern* soil profile at Kryvyi Rih area. So, the Intra-Soil Profile Differentiation Index manifested that the metal accumulations were: in the surface humus horizon for Fe, Mn, Zn, Ni, Cu, Pb (*Ispd* = 0,78–6,79) and in the intermediate humus horizon for Fe, Mn, Zn, Ni (*Ispd* = 0,71–3,38). While metals leaching dominated in the lower soils horizons: in the elluvial subsoil horizon Fe, Zn, Cu, Pb (*Ispd* = –0,31–4,06) and in the intermediate elluvial horizon Fe, Mn, Zn, Ni, Cu (*Ispd* = –3,56–6,10). Eluvial-Accumulative Index mathematical signs have shown that the HMs are segmented into two distinct groups - accumulation (for Fe, Mn, Zn, Ni, Cu *Iea* = 1,22–74,25) and leaching (for Pb and Cd *Iea* = –1,42–84,72).

The Absolute Gradient Index numerical values, as well as their modules (Table 2), indicate that in Kryvyi Rih area *Chernozems Southern* the maximum soil barrier properties are realized in the surface humus horizon (AGI = 0,01–25,26 mg/kg*cm^{-1}). In the humus intermediate horizon barrier properties are manifested somewhat less (AGI = 0,02–11,07 mg/kg*cm^{-1}). Relative Gradient Index values (Table 2) suggest that *Chernozems Southern* barrier effects cause the maximum accumulation: Fe, Mn, Zn, Ni, Cu in horizon Ahк (*RGI* = 2,16–3,71, %*cm^{-1}), in horizon ABк (*RGI* = 0,48–2,15, %*cm^{-1}) and in horizon BCк (*RGI* = 0,02–1,72 %*cm^{-1}); Fe and Mn in horizon Bк (*RGI* = 0,02–0,05, %*cm^{-1}).

In general it is necessary to note that, in Kryvyi Rih *Chernozems Southern* the humus horizon Ak is characterized by the highest total barrier effect for HMs. At that time all pedogeochemical barriers Index analysis suggests that by degree of predisposition to the soil absorption metals form next incremental series:(Cd, Pb)<<(Cu<Mn<Ni<Fe<<Mn).

Table 2
Geochemical barriers to heavy metals migration Indexes in *Chernozems Southern* soil profile at Kryvyi Rih area

Soil horizons	Fe	Mn	Zn	Ni	Cu	Pb	Cd
Intra-Soil Profile Differentiation Index (Ispd)							
Ahк	6,79	2,62	8,86	3,63	5,75	0,78	-5,59
ABк	2,56	3,38	0,71	1,04	-1,41	-1,86	-9,63
Bк	-3,24	0,13	-4,06	0,52	-0,78	-0,31	4,14
BCк	-6,10	-6,13	-5,51	-5,20	-3,56	1,39	11,08
Eluvial-Accumulative Index (Iea)							
Ahк	74,25	43,19	106,3	55,82	47,76	-4,45	-80,56
ABк	48,82	41,36	64,38	41,15	14,29	-14,57	-84,72
Bк	24,08	30,73	41,70	40,29	15,10	-9,92	-31,94
BCк	9,78	-0,55	34,48	11,69	1,22	-1,42	2,78
Absolute Gradient Index (AGI), mg/kg*cm^{-1}							
Ahк	25,26	3,46	0,46	0,49	0,12	-0,01	-0,03
ABк	11,07	2,21	0,19	0,24	0,02	-0,02	-0,02
Bк	5,46	1,64	0,12	0,23	0,02	-0,02	-0,01
BCк	3,33	0,04	0,15	0,10	0,00	0,00	0,00
Relative Gradient Index (RGI), %*cm^{-1}							
Ahк	3,71	2,16	5,32	2,79	2,39	-0,22	-4,03
ABк	1,63	1,38	2,15	1,37	0,48	-0,49	-2,82
Bк	0,05	0,02	0,00	0,00	0,00	0,00	0,00
BCк	0,49	0,02	1,72	0,58	0,06	-0,07	0,14

Thus, by our proposed for pedogeochemical barriers to chemical elements'migration indicators demonstrated very clear patterns of heavy metals vertical distribution in Kryvyi Rih area *Chernozems Southern* and *Chernozems Ordinary* soil profiles. At the same time, we believe that these regularities were exclusively caused by action of the pedogeochemical barriers to chemical elements'migration.

So for example, Contrast Index (by calculated as the ratio the metals amount in a certain soil layer to its content in the parent rock according to formula 1) clearly defined the soil layers, where there was a certain metals accumulation. Intra-Soil Profile Differentiation Index computing is more difficult because it involves carrying out intermediate compute calculus (formula 2–4). At the same time, this index very effectively demonstrates the high or low metal concentration in a certain soil horizon by comparison with its weighted average content in the soil profile.

Eluvially-accumulative Index c calculate is not complicated, but needs a correct information about the stable component content («witness») in the soil horizon and in the patterns rock (formula 5). However, this Index also very informative indicates on the metal accumulation and / or metal leaching fact in the certaine soil horizons by compared to its content in the parent rock. A priori, we suppose that Absolute Gradient Index and Relative Gradient Index manifest the intensity of the soil barriers action. In this case, these Gradient Indixes take into account the *Chernozems Ordinary* and *Chernozems Southern* soil horizons characteristics. It is important to note that Absolute Gradient Index values (calculated by the formula 6) allow analyzing the patterns only one metal within the entire soil profile distribution. While, Relative Gradient Index values (calculated by the formula 7) make it possible to compare the features of the several metals content within the entire profile of these soils.

Conclusion

Main indicators for pedogeochemical barriers to heavy metals migration are: Contrast Index, Intra-Soil Profile Differentiation Index, Eluvial-Accumulative Index, as well as Absolute / Relative Gradient Indexes. These indicators manifest that at Kryvyi Rih area *Chernozems Ordinary* and *Chernozems Southern* the pedogeochemical barriers cause heavy metal accumulation mainly in the humus horizons (surface and intermediate). Wherein, these soil barriers naturally more intensively act in Chernozem Ordinary by comparing to Chernozems Southern. In practical works, for rapid assessment of pedogeochemical migration barriers action among their indicators we recommend using mainly the Contrast Index and Relative Gradient Indexes. Since these indixes are characterized by a rather simple method of their calculations and the high information of their values. In further research it is appropriate to consider the pedogeochemical barriers dislocation patterns in soil profile on the example of Kryvyi Rih area zonal Chermozems.

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