Indicators for pedogeochemical barriers of heavy metals’ migration

V. M. Savosko

Kryvyi Rih State Pedagogical University, Kryvyi Rih, Ukraine

Article info
Received 11.01.2019
Received in revised form 18.01.2019
Accepted 27.01.2019
Kryvyi Rih State Pedagogical University,
Gagarin Avenue, 54, Kryvyi Rih, 50086, Ukraine.
Tel.: +38-097-427-10-08
E-mail: savosko1970@gmail.com

Savosko, V. M. (2019). Indicators for pedogeochemical barriers of heavy metals’ migration. Fundamental and Applied Soil Science, 19(1), 15–21. doi: 10.15421/041903

The aims of this study were to substantiate indicators for pedogeochemical barriers of heavy metals’ 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 pedosubstances 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 pedogeochemical 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 soil 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 (Aleksenko, 2003; Chertko, 2008; Kuzmin, 2000; Maksimovich, Hayrubina, 2011; Maximovich, Khayrubina, 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 pedosubstances 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).

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 index and barrier gradient index to evaluate the geochemical barriers (Perelman, 1961, 1972, 1989). In this case, the barrier contrast index is calculated as the ratio of the chemical element concentration at the barrier to its amount before 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.

![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.](image-url)

**Main pedogeochemical reactions:**
- ion exchange with the soil absorbing complex,
- fixation by humic acids,
- sorption by clay minerals,
- occlusion on surfaces of Al-Fe-Mn oxides / oxyhydroxides,
- isomorphic substitution,
- penetration into the inter-packet space of clay,
- penetration into interstice of minerals.
The pedogeochemical situation in the soil profile. Thus, the Gradient Index allows doing the following conclusions about chemical element accumulation.

\[
\text{AGI} = \frac{\Sigma(C(i) \cdot h(i))}{h(i)}
\]

Where: \(C(i)\) – metal content in i soil horizon, mg/kg; \(C(0)\) – metal content in parent rock, mg/kg; \(C_{vwa}\) – volume-weighted average metal content in soil profile, mg/kg; \(h(i)\) – i soil horizon depth, cm; \(H\) – soil profile depth, cm; \(I_{vwa\_cn}\) – volume-weighted average concentration index; \(I_{spd}\) – Intra-Soil Profile Differentiation Index; \(I_{ea}\) – Eluvial-Accumulative Index; \(R(0)\) – stable component content in parent stock, %; \(R(i)\) – stable component content 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. Nечаева (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 Indexes 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 indexes. These indices should be calculated according to formulas 6–7.

\[
AGI = \frac{Me(i) - Me(0)}{h(i)} \times 100\%
\]

\[
RGI = \frac{Me(i) - Me(0)}{Me(i)} \times 100\% \times \frac{1}{h(i)}
\]

Where: \(AGI\) – Absolute Gradient Index; \(RGI\) – Relative Gradient Index; \(Me(i)\) – metal content in \(i\) soil horizon; \(Me(0)\) – 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 profile. 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 «vertically 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 basin 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 Molisols by USA SCS (Soil Survey Staff, 2014).

Chernozems Ordinary is commonly found on the watershed plateau, rolling interfluves 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 (pH20 = 7.1–7.2), a goode developed solution neutral reaction (pH20 = 7.1–7.2), a good 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 eluvial 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

Fundam. Appl. Soil Sci., 19(1)
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).

Fig. 2. Heavy Metals Contrast Index in Chernozems layers at Kryvyi Rih area

axis abscissa – Contrast Index; axis ordinate – depth, cm;
A – Chernozems Ordinary; B – Chernozems Southern;
1 – Fe; 2 – Mn; 3 – Zn; 4 – Ni; 5 – Cu; 6 – Pb; 7 – Cd.
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 eluvial 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 (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  |
|---------------|-----|-----|-----|-----|-----|-----|-----|
| Ah            | 6,77 | 6,67 | 0,45 | -2,26 | -3,53 | -3,14 | -4,48 |
| ABk           | 13,34 | 20,73 | 13,14 | 13,98 | 18,13 | 1,88 | -7,34 |
| Bk            | -8,63 | -2,02 | -7,21 | -5,82 | -8,19 | -0,82 | 4,09  |
| BCk           | -11,48 | -25,38 | -6,38 | -5,90 | -6,40 | 2,09 | 7,73  |

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 layers (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 (AGI), mg/kg*cm⁻¹

| Soil horizons | Fe  | Mn  | Zn  | Ni  | Cu  | Pb  | Cd  |
|---------------|-----|-----|-----|-----|-----|-----|-----|
| Ah            | 21,50 | 6,08 | 0,22 | 0,22 | 0,05 | -0,03 | -0,014 |
| ABk           | 26,79 | 7,13 | 0,44 | 0,61 | 0,16 | -0,01 | -0,016 |
| Bk            | 9,14 | 5,06 | 0,09 | 0,14 | 0,02 | -0,02 | -0,006 |
| BCk           | 3,38 | 1,23 | 0,08 | 0,09 | 0,02 | -0,01 | 0,002 |

Relative Gradient Index (RGI), %*cm⁻¹

| Soil horizons | Fe  | Mn  | Zn  | Ni  | Cu  | Pb  | Cd  |
|---------------|-----|-----|-----|-----|-----|-----|-----|
| Ah            | 2,98 | 5,75 | 1,46 | 1,02 | 0,93 | -0,91 | -1,63 |
| ABk           | 3,71 | 6,74 | 2,87 | 2,83 | 3,34 | -0,35 | -1,94 |
| Bk            | 0,09 | 0,05 | 0,00 | 0,00 | 0,00 | -0,00 | 0,00 |
| BCk           | 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 layers (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 for Kryvyi Rih Chernozem Ordinary (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 eluvial 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 (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 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 eluvial 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 Chernozem 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 Ahx (RGI = 2.16–3.71, %*cm⁻¹), in horizon Abx (RGI = 0.48–2.15, %*cm⁻¹) and in horizon Bx (RGI = 0.02–1.72 %*cm⁻¹); Fe and Mn in horizon Bx (RGI = 0.02–0.05, %*cm⁻¹).

In general it is necessary to note that, in Kryvyi Rih Chernozems Southern the humus horizon Ahx 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    | Cu    | Ni    | Pb    | Cd    |
|---------------|-------|-------|-------|-------|-------|-------|-------|
| Intra-Soil Profile Differentiation Index (Ispd) |       |       |       |       |       |       |       |
| Ahx           | 6.79  | 2.62  | 8.86  | 3.63  | 5.75  | 0.78  | -5.59 |
| ABx           | 2.56  | 3.38  | 0.71  | 1.04  | -1.41 | -1.86 | -9.63 |
| Bk            | -3.24 | 0.13  | -4.06 | 0.52  | -0.78 | -0.31 | 4.14  |
| BCx           | -6.10 | -6.13 | -5.51 | -5.20 | -3.56 | 1.39  | 11.08 |
| Eluvial-Accumulative Index (Iea) |       |       |       |       |       |       |       |
| Ahx           | 74.25 | 43.19 | 106.3 | 55.82 | 47.76 | -4.45 | -80.56|
| ABx           | 48.82 | 41.36 | 64.38 | 41.15 | 14.29 | -14.57| -84.72|
| Bk            | 24.08 | 30.73 | 41.70 | 40.29 | 15.10 | -9.92 | -31.94|
| BCx           | 9.78  | -0.55 | 34.48 | 11.69 | 1.22  | -1.42 | 2.78  |
| Absolute Gradient Index (AGI), mg/kg*cm⁻¹ |       |       |       |       |       |       |       |
| Ahx           | 25.26 | 3.46  | 0.46  | 0.49  | 0.12  | -0.01 | -0.03 |
| ABx           | 11.07 | 2.21  | 0.19  | 0.24  | 0.02  | -0.02 | -0.02 |
| Bk            | 5.46  | 1.64  | 0.12  | 0.23  | 0.02  | -0.02 | -0.01 |
| BCx           | 3.33  | 0.04  | 0.15  | 0.10  | 0.00  | 0.00  | 0.00  |
| Relative Gradient Index (RGI), %*cm⁻¹ |       |       |       |       |       |       |       |
| Ahx           | 3.71  | 2.16  | 5.32  | 2.79  | 2.39  | -0.22 | -4.03 |
| ABx           | 1.63  | 1.38  | 2.15  | 1.37  | 0.48  | -0.49 | -2.82 |
| Bk            | 0.05  | 0.02  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| BCx           | 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 Chernozem Southern and Chernozem 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 compared to its weighted average content in the soil profile.

Eluvial-accumulative Index (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 indexes 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 Chernozems.

**References**

Alekseenko, V. A. (2003). Geohimicheskie bareryi [Geochemical barriers]. Logos, Moskva (in Russian).

Fundam. Appl. Soil Sci., 19(1)
Aparin, B. F., Aparin, B. F. (2012). Pochva kak biogeomembrana [Soil as a biogen-membrane]. Soil as a natural biogeomembrane: materials of the International Scientific Conference. BBM, St. Petersburg, 6–8 (in Russian).

Bradl, H. B. (2005). Heavy metals in the environment. Elsevier Academic Press, Amsterdam.

Chertko, N. K. (2008). Geoihimiya [Geochemistry]. Belorusskyi gosudarstvennyi universitet, Minsk (in Russian).

Dahabachvili, M. V., Dahabova, E. V., Titova, V. I. (2005). Tyazhelye metally: ekotoksikologiya i problemiy mi normirovaniya [Heavy metals: Ecotoxicology and normalization problems]. Izdatelstvo VVAGS, Nizhny Novgorod (in Russian).

Dobrovolskiy, V. V. (1997). Biosferennye tsikly tyazhelyih metallei i regul'atornaya rol pochvyi [Biospheric cycles of heavy metals and the regulatory role of soil]. Eurasian Soil Science, 4, 431–441 (in Russian).

Dobrovolskiy, H. V., Nkkyttyn, E. D. (2000). Sokhranenye pochv kak nezamenyomogo komponenta byosferu [Soil conservation as an indispensable component of the biosphere]. Nauka, Moskva (in Russian).

Dolina, O. O., Smetana, O. M. (2014). Territorionalna struktura ta klassifikatsiya gruntiv Krivorizkogo zaliznorudnogo bassejnu [Territorial pattern and classification of soils of Kryvyi Rih Iron-Ore Basin]. Visnyk of Dnipropetrovsk University. Biology, ecology, 22(2), 161–168 (in Ukrainian).

Fridland, V. M. (1981). Chernozemy SSR [Chernozems of the USSR]. Kolos, Moscow (in Russian).

Gedroyts, K. K. (1955). Uchenie o poglotitelnoy sposobnosti pochv [The doctrine of the absorption capacity of soils]. Selected works in three volumes. Volume one. Agricultural Literature Publishing House, Moscow. 241–384 (in Russian).

Glazovskaya, M. A. (1988). Geoihimiya prirodnih i tehnogennih landshtaf SSR [Geochemistry of natural and man-made landscapes of the USSR]. Vyisshaya shkola, Moskva (in Russian).

Kopcik, G. N. (2014). Sovremennye podhody k remediacii pochv, zagryaznennyh tyazhelyymi metallyami (obzor literatury) [Modern approaches to remediation of soils contaminated by heavy metals (literature review)]. Eurasian Soil Science, 7, 851–868 (in Russian).

Kossovich, P. S. (1916). Kratkii kurs obshego pochvovedeniya [Short Course of General Soil Science]. Printing house Altshuler, Petrograd (in Russian).

Kuzmin, V. A. (2000). Geoihimiesskiye bareryi v pochvah Pribyalkalya [Geohchemical barriers in the soils at Baikal region]. Eurasian Soil Science, 10, 197–102 (in Russian).

Maksimovich, N. G., Hayrunina, E. A. (2011). Geoihimiesskiye bareryi i ohrana okruzhayushchee sredyi [Geohchemical barriers and environmental protection]. Permskiy gosudarstvennyi universitet, Perm (in Russian).

Maximovich, N., Khayrulina, E. (2014). Artificial geochemical barriers for environmental improvement in a coal basin region. Environmental Earth Science, 72, 1915–1924.

Motuzova, G. V. (2009). Sostojeniyami mikroelementov v pochvakh: sistemnyaya organizatsiya, ekologicheske znachenie, monitoring [The compounds of trace elements in soils: system organization, ecological significance, monitoring]. Knizhnyiy izdatelstvo, Moskva (in Russian).

Nechaeva, E. G. (1985). Landshtafno-geoihimiesskiye analiz dinamiki taezhnyih geosistem [Landscape-geochemical analysis of dynamics of taiga ecosystems]. Institute of Geography of the Siberian Branch of the Russian Academy of Sciences, Irkutsk (in Russian).

Perelman, A. I. (1961). Geoihimiya landshafta [Landscape Geochemistry]. Gosudarstvennoe izdatelstvo geograficheskoy literatury, Moskva (in Russian).

Perelman, A. I. (1972). Geoihimiya elementov v zone gipergeneza [Geochemistry of elements in the hypergenesis zone]. Nedra, Moskva (in Russian).

Perelman, A. I. (1989). Geoihimiya [Geochemistry]. Vyisshaya shkola, Moskva (in Russian).

Rode, A. A. (1937). Podzoloobrazovatelnyj process [Podzol formation process]. Publishing house of Sciences Academy of USSR, Moscow-Leningrad (in Russian).

Savosko, V. M. (2003). Gidrotehnogennoe nakoplenie podvizhnyih form tyazhelyih metallei v pochvah Krivbassa [Hydrotechnogenic accumulation of heavy metals mobile forms in soils at Kryvyibrass]. Gruntoznovastvo, 4(1–2), 105–109 (in Russian).

Savosko, V. M. (2009). Lokalnoe fonovoe soderzhanie tyazhelyih metallei v pochvakh Krivorizhskogo zhelezorudnogo regiona [The heavy metals local background contents in soils at Kryvyi Rih iron ore region]. Gruntoznovastvo, 10(3–4), 64–73 (in Russian).

Savosko, V. M. (2015). Gruntovyy pokryv Kryvorizhzya [The Soil Cover at Kryvyizhy]. Fizicha geografiya Kryvorizhzya – monografichna navchalna kniga [Physical geography of Kryvorizhzya – monographic educational book]. Published Roman Kozlov, Kryvy Rih (in Ukrainian).

Savosko, V. N. (2016). Tyazhelye metallyi v pochvah Krivbassa [Heavy metals in soils at Kryvyibrass]. Dionat, Krivy Rog (in Russian).

Savosko, V. M. (2017). Genesiz ideyi ta definicinya pedogeochemichnih bar'yeryv migracji vazhkih metallyv [Genesis’idea and definition for pedogeochemical barriers of heavy metals’migration]. Gruntoznovastvo, 17(3–4), 21–29 (in Russian).

Simonov, G. A. (2004). Balansovyy metod issledovaniya mineralnoy massy pochvy [Balance method for studying the mineral mass of soil]. Vestnik Instituta biologii KomI NC URO RAN 46–49 (in Russian).

Sposito, G. (2008). The Chemistry of Soils. Oxford University Press, New York.

Tan, K. H. (1982). Principles of soil chemistry. Marcel Dekker Inc, New York.

World reference base for soil resources, 2014. International soil classification system for naming soils and creating legends for soil maps. Food and Agriculture Organization of the United Nations, Rome.

Polupan, M. I., Solovey, V. B., Velichko, V. A. (2005). Classification of soils at Ukraine. Agrarian Science, Kyiv (in Ukrainian).

Soil Survey Staff, 2014. Keys to Soil Taxonomy, 12th Edition. USDA-Natural Resources Conservation Service, Washington.

Vaselev, A. A., Chaschin, A. N. (2011). Tyazhelye metallyi v pochvah goroda Chusovoy: otsenka i diagnostika zagryazneniy [Heavy metals in the soils at Chusovoy city: assessment and diagnosis of pollution]. Permskaya GSHA, Perm (in Russian).

Verander, N. B., Gogolev, I. N., Kovalishinb, D. I., Novakovskij, L. Ya., Sirenvo, N. A., Tytuny, D. A., 1986. Priroda Ukrainskoj SSR, Tom Pochvy [Nature of the Ukrainian SSR, Volume Soils]. Naukova Dumka, Kyiv (in Russian).

Fundam. Appl. Soil Sci., 19(1)

21