RESEARCH PAPER

# VERTICAL AND SPATIAL DISTRIBUTION OF MAJOR AND TRACE ELEMENTS IN SOIL CATENA AT THE CENTRAL FOREST STATE NATURE BIOSPHERE RESERVE (SE VALDAI HILLS, RUSSIA)

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ABSTRACT. In this study, we discussed relationship between the vertical and spatial differentiation of 14 chemical elements (total content and three mobile fractions extracted by $NH_4Ac$, $NH_4Ac$ with 1% EDTA and 1M $HNO_3$) and the environmental factors in background Retisols and Stagnosols within a soil catena. In the A soil horizon, the extractability of elements decreased in the series Cd, Mn, Pb> Co, Ni, Cu, Fe> Zn, Bi, As> U, Cr, Mo> Sb. In the O and A horizons, total and exchangeable Mn and Zn were uptaken by plants. In the A horizon, total Bi, Cd, Pb, Sb, Mo, exchangeable As, Bi, Cd, Co, Ni, Mo, as well as As, Cd, Cu, Pb, Zn, Sb bound with Fe-Mn (hydr)oxides were sorbed by soil organic matter; Cr, Fe, Mn formed the organic complexes. In the C horizon, Cd, Fe, Mn, Sb complexes co-precipitated with carbonates. In the Bt horizon, total Cr, Cu, exchangeable Cu, Ni, as well as Cr and U bound with Fe-Mn (hydr)oxides migrated due to the lessivage. On the toeslope's biogeochemical barrier, exchangeable Zn, Mo bound with complexes, As, Bi, and Fe bound with Fe-Mn (hydr)oxides were accumulated. In the lower part of the catena, peat accumulated the exchangeable compounds of As, Bi, Cr, Fe, Mo, Pb, U. The spatial differentiation of elements became less contrasting from the O and A horizons to the E, B and C horizons.

KEYWORDS: heavy metals and metalloids; fractionation; geochemical barrier; mobility; environmental assessment; protected area

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## INTRODUCTION

Vertical and spatial geochemical differentiation (structure) of landscapes depending on the vertical and lateral flows of compounds in catenas is described using different geochemical ratios. The distribution of substances in landscapes could be explained using the concept of geochemical barriers, i.e. areas where the mobility of chemical elements sharply decreases over a short distance, leading to their accumulation in various forms (Kasimov, Perelman 1992). The vertical geochemical differentiation of landscapes depends on the location of geochemical barriers in the soil horizons. These are biogeochemical, sorption, gley, and, more rarely, carbonate barriers in forest soils (Kasimov, Perelman 1992). The spatial geochemical differentiation of landscapes depends on the contrasting changes of the environments for lateral flows of substances in catenas (Kasimov et al. 2012). A spatial sorption-biogeochemical barrier is the most common in taiga catenas (Avessalomova and Mikliayeva 1997; Samonova et al. 2011; Semenkov et al. 2016; 2019). Coupled analysis of the vertical and spatial distribution of elements depending on the properties and environmental factors depicts the migration ability of elements (Kasimov and Gennadiev 2005).

When characterizing the conditions of migration and accumulation of heavy metals and metalloids (HMMs), the analysis of their total content is usually complemented by the fractionation, closely related to mobility which is often estimated in terms of extractability, i.e. the transition of compounds from soil to solution under the action of various reagents (Burachevskaya et al. 2020; Shao et al. 2020; Sungur et al. 2021). The extracted fractions of HMMs are referred to as F1, F2, F3 in order of their recovery from the solid phase, i.e. decreasing extractability. Water-soluble and exchangeable fractions (F1) are considered to be the most mobile and available to plants (Minkina et al 2018). Fractions bound with complexes (F2), including carbonate and organomineral compounds, are the closest pool available to plants (Minkina et al 2018). Compounds bound with Fe and Mn (hydr)oxides (F3) are mobile only in a gley environment (with a low redox potential), as well as under the long-term exposure to acid exudates of plants. Silicates are usually considered as a residual fraction (F4), the compounds of which are unavailable to plants and move only as a result of mechanical migration (Minkina et al 2018). The ratio of F1+F2+F3 to the total content reflects the mobility of HMMs in soils (Yutong et al. 2016). The F-analysis is a modern approach to studying the migration of chemical elements in soils and landscapes (Bolan et al. 2014; Li et al. 2019; Reimann et al. 2018; Sosorova et al. 2012; Gronflaten, Steinnes 2005; Semenkov et al. 2016, 2019; Huang and Matzner 2007; Sosorova et al. 2012; Motuzova 2014; Popova 2010; Kosheleva et al. 2002, 2015).

As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, U and Zn selected for the study are from different groups of chemical elements (Fig. 1). They differ according to the preferred host phases (Goldshmidt 1924), migration features in surface waters (Krainov et al. 2012), and in plants (Perelman, Kasimov 1992).

Fractionation is commonly used to assess phytoavailability, so the most of HMMs occurrence patterns are studied within agricultural landscapes. Thus, the LUCAS (Land Use/Cover Area frame statistical Survey) and GEMAS (Geochemical Mapping of Agricultural Soil) European projects analyze the Ap-horizon (Reimann et al. 2018). In recent years in the international environmental programs of UNESCO and UNEP, special attention is paid to the assessment of background landscapes, which is mainly carried out in biosphere reserves. The studies of vertical differentiation of the element mobile fractions in Retisols show that F1 fractions of Zn, Mn, Fe (Sosorova et al. 2012), F2 fractions of Mn, Pb, Mo (Gronflaten, Steinnes 2005; Semenkov et al 2016) and F3 fractions of As, Mn, Zn, Co, Pb (Semenkov et al 2016) accumulate in the A-horizon at the biogeochemical barrier. F1 fractions of Ni, Pb, As, Cu (Huang and Matzner 2007; Sosorova et al. 2012; Motuzova 2014), F2 fractions of Zn (Popova 2010) accumulate at the sorption geochemical barrier in the A- and Bt-horizons and is depleted in the E-horizon. F3 fractions of Fe, Co, Cr, Cu (Tolpeshta and Sokolova 2010; Semenkov et al 2019; Adriano 2001) are removed from the topsoil. Their content increases monotonously in the subsoil horizons.

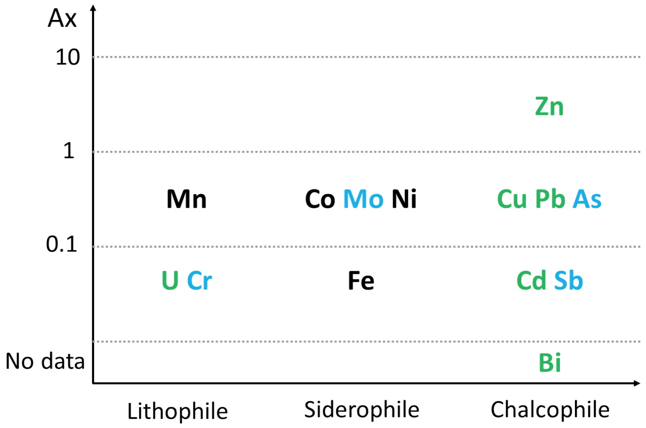


**Fig. 1. Groups of chemical elements according to the main migration properties. The classification of Goldschmidt (1924) is displayed on the horizontal axis. The vertical axis shows the values of the Ax index (Perelman, Kasimov 1999) the ratio of the content of an element in the plant ash to the content in the parent rock. The prevailing form of migration in surface waters are shown in color (Kraynov et al. 2012): green – complex, black – cationic and complex, blue – anionic**

Few studies of spatial differentiation of element mobile fractions in background taiga landscapes show that F1 fractions of Cu, Zn, Mn, Co and F2 fractions of Cu, Co accumulate in the upper parts of the catenas (Semenkov et al. 2019; Semenkov et al. 2016). The content of F1 fractions of Ni Co, Fe, F2 fractions of Fe, Zn, Ni, Sr, Pb and F3 fractions of Fe, Mn, Cr и Ni increases down the catena (Kosheleva et al. 2002; Semenkov et al. 2019; Semenkov et al. 2016).

Coupled studies of vertical and spatial differentiation of various compounds of HMMs, which are in demand for the environmental assessment, are uncommon. Such a coupled analysis of the chemical composition of landscape components of background ecosystems in ecological monitoring is necessary for solving theoretical and applied problems of landscape geochemistry.

The aim of the work is to determine the environmental factors affecting the vertical and spatial distribution of As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, U and Zn fractions and their mobility in background Retisols and Stagnosols within a soil catena located in the Central-Forest Natural Reserve with coniferous-broadleaved southern taiga landscapes. The following tasks were solved: 1 – the average concentration of chemical element mobile fractions were evaluated in background soils; 2 – chemical elements extractability and proportion of fractions were identified in each genetic horizons; 3 – geochemical barriers in soil horizons which affect the vertical distribution of chemical elements fractions in soils were determined; 4 – geochemical barriers in soil catena landscapes which affect the spatial distribution of chemical elements fractions were found.

## MATERIALS AND METHODS

### Object of study

The survey was taken within the Central Forest Nature Biosphere Reserve, (Fig. 2), located in the Valdai Hills. The background southern taiga landscapes of the Central Forest Nature Reserve were chosen, because here we can study the migration of HMMs between landscape components in natural conditions. Here, the structure, dynamics and functioning of the reference ecosystems of the southern taiga is monitored. Which makes it possible to study the background soil-geochemical structure of the catenas of the region in more detail. In addition, the data getting from the Central Forest Nature Reserve territory can be used for a comparative analysis of pollution levels in the Moscow region.

A 187 m long soil catena was studied on the southeastern gentle (<2º) slope in the southern part of the Central Forest Nature Reserve protected area. It begins at the top of a hill at 265 m a.s.l., crosses the slope and ends in a small gully on a flat terraced surface (Fig. 3). Despite small slopes and short distance, soils and vegetation change drastically (Fig. 3, Table 1) due to the repartitioning of surface water. The summit and the backslope of well-drained hill are covered by coniferous-broadleaved forest on Albic Stagnic Retisols with O–OA–E–BE–Bt–BC and O–OA–Ah–AE–E–BE–Bt–C horizons, respectively (Table A.1, Fig. 2). The coniferous-broadleaved forest on Endocalcaric Glossic Albic Gleyic Histic Stagnosols with O–H–A–Eg–Btg–Cg-horizons covers the footslope, too. The toeslope position of a bogged gully with a temporary stream is occupied by coniferous forest on Endocalcaric Glossic Albic Histic Stagnosols with O–H–Eg–Btg–Cg-horizons. The parent rocks are mantle loams underlain by carbonate moraine loams at a depth of 90-190 cm deposited during the Valday (MIS-2) glaciation

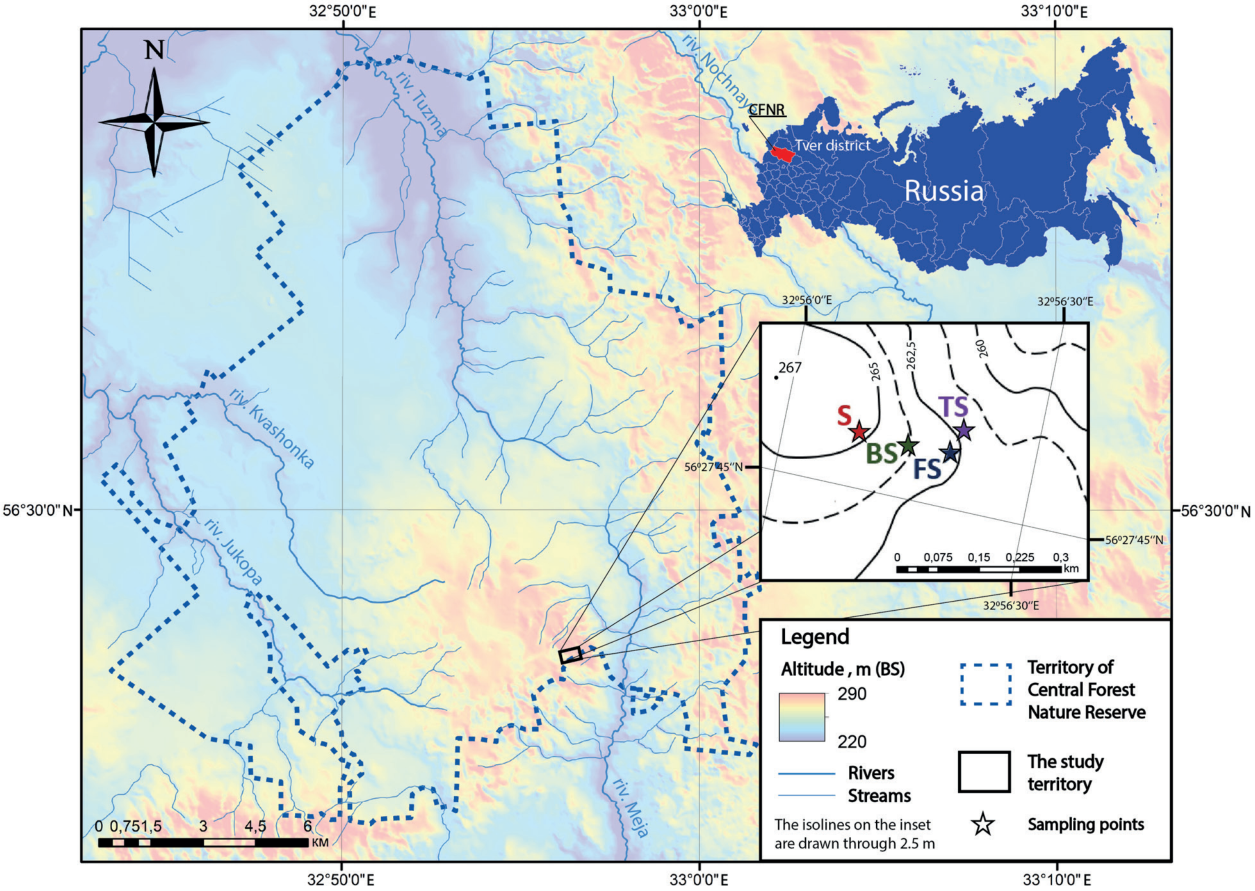


**Fig. 2. Study object location. Toposequence in the Central Forest Nature Reserve; positions (hereinafter in the figures and tables): S – summit (interfluve); BS – backslope; FS – footslope, TS – toeslope**

(Karavanova and Malinina 2009; Puzachenko et al. 2013). Due to the low water permeability of parent rocks, the toeslope position is waterlogged (Puzachenko et al. 2013). According to I.S. Urusevskaya (1990), the catena is a subordinate hydromorphic soddy-podzolic-marsh one. According to N.S. Kasimov et al. (2012), it is a typical monolithic watershed-marsh catena from the autonomous summit landscape to the superaqueous one at the bottom of a temporary watercourse with a relatively uniform composition of soil-forming rocks (binary: mantle loams on moraine).

## Research methods

In the last decade of June 2017, 30 samples were taken from all soil horizons (Table 1). The pH value in suspension was measured on the Expert-pH pH-meter under static conditions (error ±0.07 pH units). The soil organic matter (SOM) content was determined by titrimetry using the bichromate oxidation method. The granulometric composition was analyzed on the Analysette 22 comfort laser granulometer (Fritsch, Germany) separating seven granulometric fractions (Kachinsky 1958): clay (<1 µm); fine, medium and coarse silt (1–5, 5–10, and 10–50 µm,

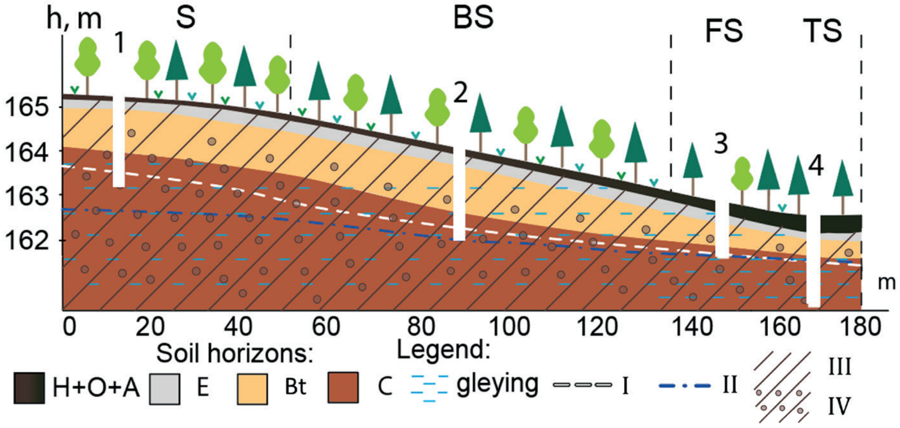


**Fig. 3. Toposequence of soils: 1 – Summit position – Endocalcaric Albic Neocambic Stagnic Glossic Retisols under coniferous-deciduous forest; 2 – Backslope position – Endocalcaric Albic Neocambic Stagnic Glossic Retisols under coniferous-deciduous forest; 3 – Footslope position – Endocalcaric Glossic Albic Gleyic Histic Stagnosols under coniferous-deciduous forest и 4 – Toeslope position – Endocalcaric Glossic Albic Gleyic Histic Stagnosols under coniferous forest. Horizons: O – organic, H – histic, A – humus, E – albic, Bt – argic, C – parent material. I – upper boundary of effervescence with 10% HCl; II – ground water level, III – mantle like loams, IV – carbonate moraine deposits**

respectively); fine, medium and coarse sand (50–250, 250–500 and 500–1000 μm).

Mobile fractions of elements were extracted by the method of parallel extraction (Minkina et al. 2018) with incubation for 18 hours with solutions of $NH_4Ac$ with pH 4.8, $NH_4Ac$ + 1% EDTA with pH 4.5 (soil to solution ratio 1:5) and 1M $HNO_3$ (soil to solution ratio 1:10). An exchangeable fraction (F1), represented by easily and moderately soluble salts and complexes, was extracted with $NH_4Ac$. The fraction of compounds bound with carbonate or organic complexes (F2) corresponded the difference in the content of elements in $NH_4Ac$ + 1% EDTA and $NH_4Ac$ extracts. The fraction of compounds bound with Fe-Mn (hydr)oxides (F3) was calculated as the difference in the content of elements in 1M $HNO_3$ and $NH_4Ac$. An open system acid digestion method was used for the dissolution of soil samples prior to the total elemental analysis (Karandashev et al. 2017). 5% of all samples were measured in duplicates. The content of chemical elements in solutions was measured using the Elan-6100 ICP-MS System and the Optima-4300 DV ICP-AES System. Blank solutions of $NH_4Ac$, $NH_4Ac$+1% EDTA and 1M $HNO_3$ were analyzed, too.

Mobility, as a set of loosely bound fractions, is the total proportion of exchangeable (F1), complex (F2), and sorbed by Fe-Mn (hydr)oxides (F3) fractions in the total content of an element (Bolan et al. 2014; Li et al. 2019). Basing on the mobility (%), the HMMs are divided into low mobile <5, moderately mobile 5-25, mobile 25-50, and highly mobile >50.

Based on the chemical and morphological properties of the horizons, biogeochemical, sorption (by soil organic matter, silt particles, Fe-Mn nodules) and alkaline geochemical barriers were identified in the studied soils. The alkaline barrier was implemented through an increase in pH value and carbonate content in Bt and C-horizons. The biogeochemical barrier characterized of the topsoil with a high content of soil organic matter. The sorption barrier appeared in case of increasing of the content of the clay fraction in the Bt-horizon or Fe-Mn nodules in the E and Bt-horizons. The possibility of accumulation of HMMs at the geochemical barrier was diagnosed according to two criteria: i. an increase in the content of chemical element fraction in the soil horizon; ii. the existence of a positive significant correlation with the soil property, which can be an indicator of a particular geochemical barrier (Semenkov and Koroleva 2020, Kosheleva et al. 2015). We understand that it is impossible to unambiguously confirm or refute the accumulation of chemical elements fractions on the geochemical barrier by the presence or absence of a significant correlation with indicator soil properties. However, in the studied soils, we have identified properties and barriers that are more likely to determine the formation of certain patterns vertical partitioning of chemical elements.

The correlation analysis of the content of elements and the physicochemical properties of soils was carried out using the STATISTICA program. The accumulation of elements at geochemical barriers was justified by the presence of a significant ($p<0.05$) Spearman rank correlation ratios (r) between the contents of HMMs and soil properties calculated using the whole data set obtained. The relationship with the pH value indicates the presence of an alkaline barrier; a sorption barrier is associated with the content of clay fraction (<1μm), and a biogeochemical barrier is associated with the content of SOM. The variable content of fractions of chemical elements in the A-horizon was evaluated using the coefficients of variation (Cv) calculated based on the data on the A horizon in all cross-sections.

The regional geochemical specialization of soils was estimated using element abundances (CC), i.e. the ratio of the total contents of HMMs in soils and their concentrations in the upper part of the continental Earth's crust (Rudnick and Gao 2003), and concentration coefficients (Cc), i.e. comparisons of the contents of mobile (F1, F2, F3) fractions of HMMs in soils with average values reported for the A-horizon of the Retisols at the East European Plain and the Albic Luvisols of Western Siberia (Samonova et al. 2018, Semenkov et al. 2019; Semenkov et al. 2016). As a Cc ranged from 0.5 to 2.0, the content of elements was similar with the standards. Since the territory of the reserve is far from sources of pollution, the main reason for going beyond these limits was considered to be the local natural peculiarities of soils and rocks.

To characterize vertical and spatial distribution of As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, U and Zn, varied ratios were calculated. Accumulation and dispersion of HMMs in the soil horizons (Chor) relative to the rock (Crock) was diagnosed using the coefficient (1) of vertical differentiation R (Kasimov and Perelman 1992):

$$R = Chor / Crock \qquad (1)$$

The spatial differentiation was described using the coefficient L (2) characterized the difference between soils located on the slope (Csub) and soils sampled in the interfluve (Cint) (Kasimov and Perelman 1992):

$$L = Csub / Cint \qquad (2)$$

When the coefficients R and L exceed 2.0, the element was considered to be concentrating. If it was less than 0.5, the element was considered as dispersing. According to Rozanov (2004), four types of the element vertical distribution in soils were identified: (i) accumulative, with maximum concentration of an element in the A-horizon and monotonic decrease with depth due to accumulation at the biogeochemical barrier; (ii) accumulative-eluvial-illuvial, with accumulation at the sorption geochemical barrier in the A- and Bt-horizons and removal from the E-horizon; (iii) eluvial, with removal from the topsoil and monotonous increase in concentration in the subsoil horizons; (iv) ground-accumulative, with removal from the upper and middle part of the profile and residual accumulation in the soil-forming rock, or accumulation on the alkaline geochemical barrier.

## RESULTS AND DISCUSSION

### Soil properties

Retisols and Stagnosols of the southern taiga catena have clearly distinguishable E- and Bt-horizons, and eluvial-illuvial type of clay fraction distribution (Table A.1). The development of soils on binary sediments is confirmed by E-horizon enriched in silt fractions, and by Bt-horizon and parent rock enriched in clay fraction (Fig. 4), which is typical for the Central Forest Nature Reserve territory (Puzachenko et al. 2013), for similar soils of Karelia (Lukina et al. 2019) and Tobolsk Upland (Semenkov et al. 2019). The pH value varies from strongly acidic (pH=3.7) in the topsoil horizons (Table 1) to slightly alkaline (pH=7.5) in the C-horizon, which corresponds to the parameter spread in Albeluvisols in the Central Forest Nature Reserve (Sokolova et al. 2014). The SOM content decreases sharply with depth, which is also typical of taiga soils (Lukina et al. 2019). In general, the studied soils of the southern taiga catena have all features and parameters specific to texture-differentiated soils of southern taiga landscapes on mantle loams underlain by a carbonate moraine.

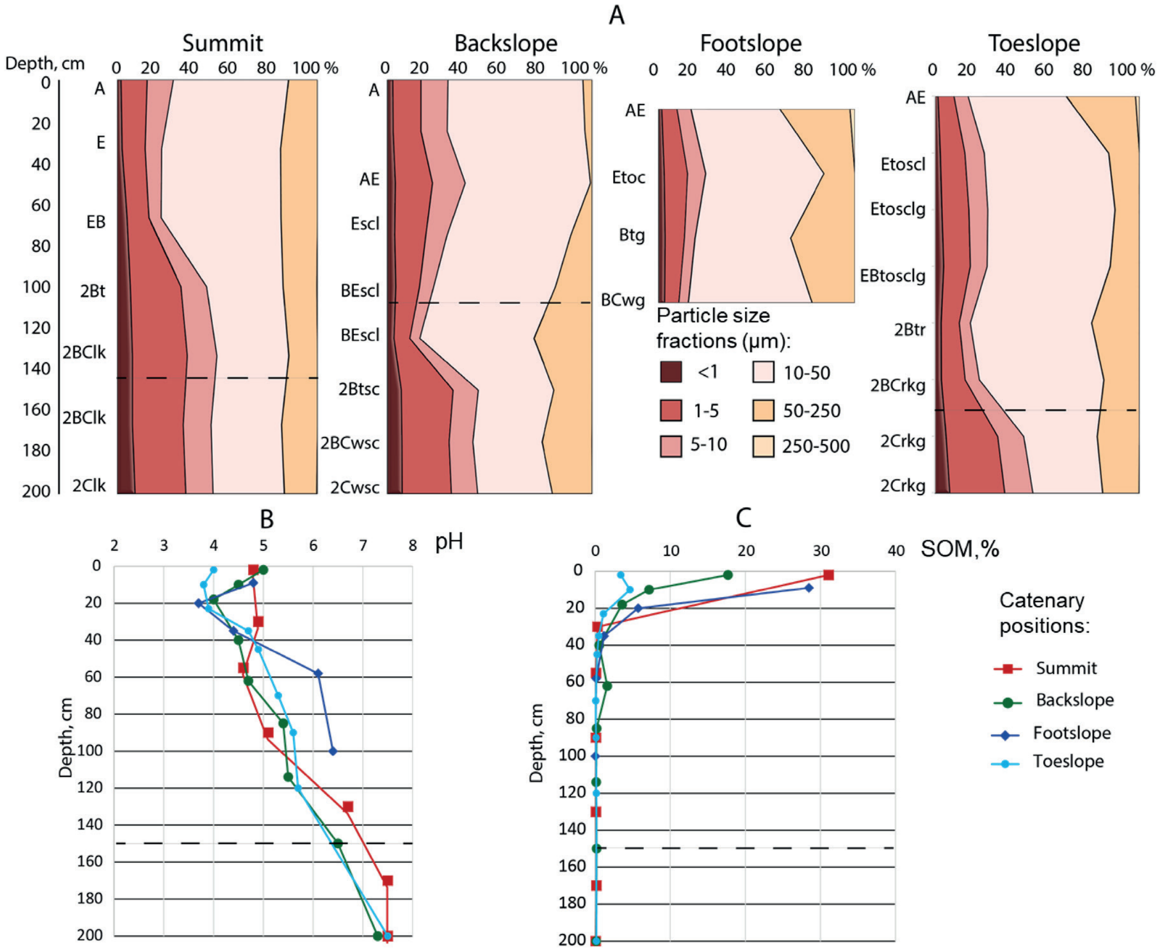


**Fig. 4. The vertical differentiation of the Retisols studied. A – granulometric fractions in μm. B – pH value. C – SOM. Dotted line – upper boundary of effervescence with 10% HCl**

## Average concentration of chemical elements

*Total content.* Elemental composition of the A-horizon of soils studied differs slightly with the upper continental Earth's crust (subscript is for CC): Bi$_{1.8}$ Sb$_{1.6}$ Zn$_{1.1}$ Mn$_{0.7}$ Mo$_{0.6}$ U$_{0.5}$. The reduced content of As Cu$_{0.4}$ Cr Co Fe Ni$_{0.2}$ is due to lower concentration of the elements in the mantle loam, which was also noted (Avessalomova 2017). Higher content of Cd$_7$ in the A-horizon can be explained by its uptake by woody plants and that of Pb$_2$ by its accumulation in *Picea abies* needles (Enchilik et al. 2020). The total content of most elements (Bi, Co, Cr, Cu, Mn, Mo, Ni, U and Zn) in the A-horizon of studied soil is similar (Fig. 5) to the data on agricultural soils in Europe (Reimann et al. 2018). The content (subscript is for Cc) of As$_{0.3}$ and Fe$_{0.4}$ is slightly reduced, and that of Cd$_{3.5}$ Sb and Pb$_{2.2}$ is increased. The increased content of Cd and Pb results from participating of the elements in the biological cycle of woody plants (Enchilik et al. 2020). Sb is a component of humic acids (Kabata-Pendias and Szteke 2015), which are insoluble under acidic conditions. The total elemental composition of the E-, Bt- and BCk-horizons of soils studied differs slightly with the upper continental Earth's crust. (Table 1). According to variability of the total content (subscript index - *Cv*, %), the elements form the following series: Mn$_{73}$> Cd$_{55}$ Zn Ni$_{51}$ Sb$_{47}$ Bi$_{41}$ Fe$_{40}$ As$_{37}$ Mo$_{33}$ Pb$_{32}$ Cr, Co$_{28}$ U$_{22}$ and Cu$_{19}$. It means that the total content of most elements in the A-horizon shows low to medium variability. Based on the data on the environmental conditions, phisyco-chemical properties and elemental composition, we think that the studied catena can be considered as background for the purpose of regional soil geochemical monitoring in the center of the East European Plain.

*Exchangeable fraction (F1).* The content of exchangeable (subscript is for Cc) Mn As$_{>100}$ Ni Fe$_{>10}$ U$_7$ Cd Cr$_5$ Pb, Zn$_4$ (Fig. 5, Table 1, Table A.3) in the A-horizon is higher than their average concentration in background Albic Luvisols (Semenkov et al. 2019). Essential Mn and beneficial for plants Pb and Cr are fixed by organic matter at the biogeochemical barrier (Table A.5). Zn is involved in the synthesis of chlorophyll (Boyd, 2020; Kabata-Pendias and Szteke 2015) and accumulates in the acid A-horizon with the litter of photosynthetically active plant organs (Enchilik et al. 2020) due to immobilization by soil microorganisms (Perelomov and Chulin 2014) and sorption by organic matter. Increased content of Mn, Ni, Fe, Pb, and Zn relative to soils of the Tobolsk Upland (Semenkov et al. 2019) could be also due to the lower degree of gleying of the studied soils and, as a result, more favorable conditions for elements preservation in the A-horizon. The content of Fe$_{2.3}$ and Zn$_{4.1}$ Ni$_{2.6}$ Mn$_{2.0}$ in the E- and Bt-horizons, respectively, is higher than in the soils of the Mezen-Vychegda Plain (Semenkov et al. 2016) which could be supported by the change of redox conditions and the formation of a complex redox barrier in these horizons under poorly-permeable soil-forming rocks and the proximity of groundwater in the lower part of the catena. The content of Fe$_{16}$ Mn$_{11}$ Co$_{10}$> Zn$_5$ Cd$_4$ Ni$_3$ in carbonate horizons is higher than in soils of the Mezen-Vychegda Plain (Semenkov et al. 2016) since the elements accumulate at the contrasting carbonate barrier under higher pH values (Fig. 5). The accumulation of exchangeable Co and Ni at the alkaline barrier is in accordance with a positive correlation with $CaCO_3$ content (Table A.5).

Variability of the content of F1 of elements (subscript is for *Cv*, %) is higher than that of the total content: Mo Fe As U Cr$_{100}$ Mn$_{97}$> Zn$_{70}$> Co$_{54}$ Pb Bi$_{47}$> Cd$_{38}$ Cu$_{33}$ Ni$_{28}$.

*Fraction bound with complexes (F2).* The content of complexes of $Pb_{15}$ $Bi_{10}$>$Cu_{8.4}$ $Mo_{4.4}$ in the A-horizon (Fig. 5, Table 1, Table A.3) exceed the data available in the literature (Semenkov et al. 2019), apparently due to the regional biogeochemical specialization of plants of the Valdai Hills, which accumulate these elements in their aerial tissues (Enchilik et al. 2020). F2 compounds could migrate as a part of dissolved organic matter and organic complexes (Moiseenko et al. 2013). In the E-horizon, concentration of $Cd_{0.4}$ $Fe_{0.3}$ $Mn_{0.2}$ $Cu_{0.1}$ (subscript is for *Cc* values) is lower than in Luvisols of the Mezen-Vychegda Plain, probably due to the lower proportion of clay fraction in the studied soils; and the content of Pb is the only one higher (Fig. 4, Table A.2). Concentration of $Cd_{59}$> $Cr_9$ $Ni_{4.4}$ $Zn_{4.2}$ $Pb_3Co_{2.7}$ in the Bt-horizon is higher than in more acidic Bt-horizon sampled in the Mezen-Vychegda Plain; and that of $Cu_{0.3}$ is lower probably due to the lower content of clay fraction in the studied Retisols which shows positive correlation with the element (Table A.5). The content of F2 of $Ni_4$ is the only one increased in the BCk-horizon. According to variability of the content of F2 (subscript is for *Cv*, %), the elements form the series: As Mn $Fe_{100}$ $Sb_{96}$> $Mo_{82}$ $Zn_{78}$ $Cr_{74}$> $Co_{51}$> $Cd_{39}$ $Cu_{36}$ $Ni_{33}$> $Bi_{17}$ $Pb_{13}$.

*Fraction bound with Fe-Mn (hydr)oxides (F3).* In A-horizon, the content of $Mn_{0.4}$ Fe Bi $Cd_{0.3}$ As $Co_{0.1}$ Ni Cr Mo Sb $U_{<0.1}$ (subscript is for Cc values; Fig. 5, Table 1) is lower than in soils of the Tobolsk Upland (Semenkov et al. 2019), where gleying is more intense. Retisols (Loamic) of the middle and southern taiga are enriched with F3 of elements in the lower part of the E-horizon (Sokolova et al. 2014). For example, the content of F3 of $Mn_{2.2}$ $Pb_{1.6}$ and $Ni_{8.1}$ $Mn_{1.6}$ in the E- and Bt-horizons of the studied Retisols, respectively is increased relative to the soils of the Mezen-Vychegda Plain. The concentration of $Ni_{2.4}$ slightly increases in the carbonate horizon probably due to higher pH values (Fig. 4) than in the same soil horizons within the Mezen-Vychegda Plain (Semenkov et al. 2016). According to the variability of the content of F3 (subscript is for *Cv*, %), the elements form the series: Bi Sb $Mn_{100}$ $Cr_{98}$ $U_{92}$ $Zn_{85}$ $Co_{82}$ $Cd_{77}$> $Fe_{52}$ $Ni_{51}$> $Pb_{43}$ $As_{39}$ $Cu_{35}$.

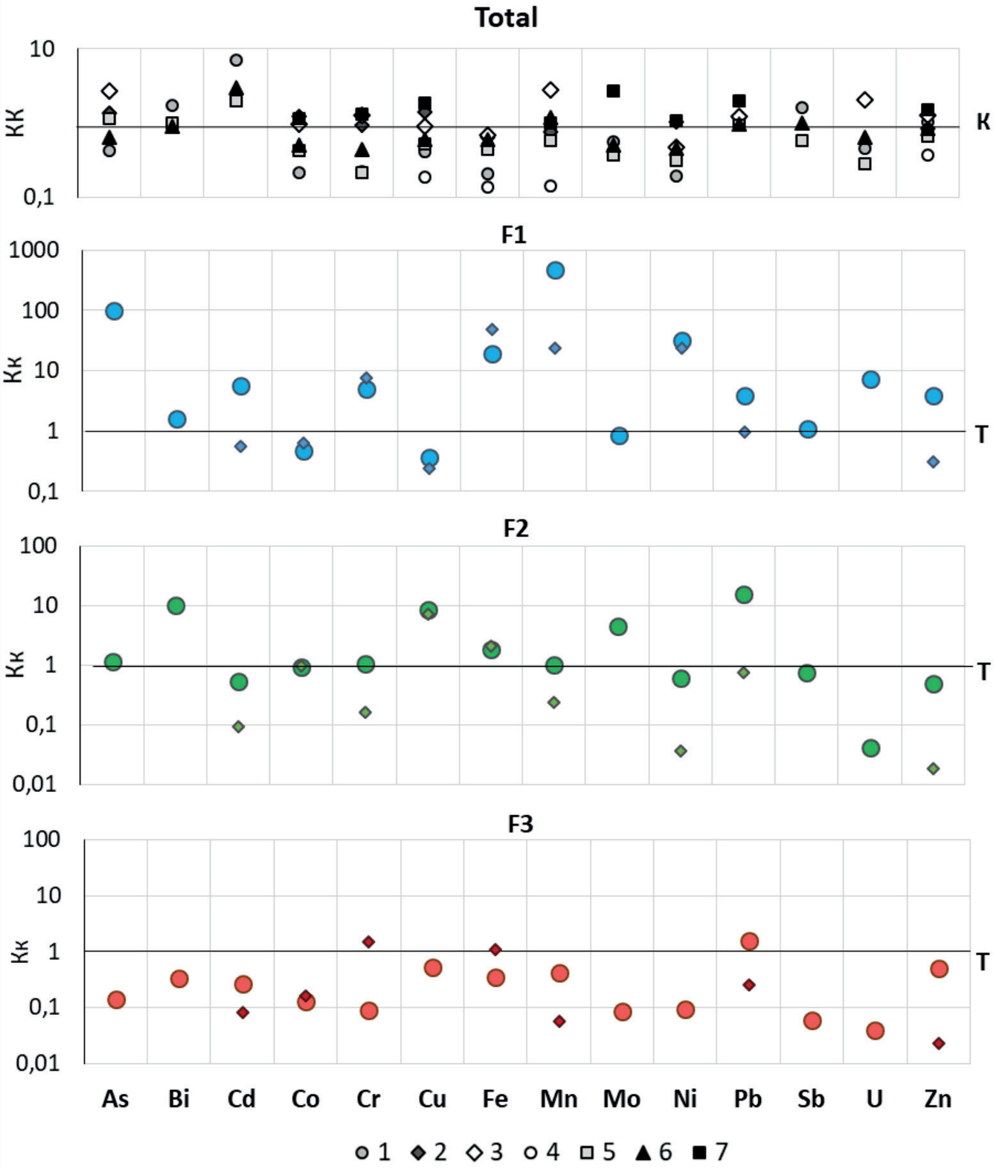


**Fig. 5. Differences in average element concentrations in the humus horizons of the site and background datasets. Total element content is normalized to element abundances of the upper part of the continental Earth's crust (Rudnick and Gao 2003), mobile fractions (F1, F2, F3) content is normalized to Albic Luvisols in the Tobolsk upland (Semenkov et al. 2019). Soils:1 – Albic Retisols and Stagnosols in the Central Forest Nature Reserve (present study), 2 – Albic Retisols in the Mezen-Vychegda Plain (Semenkov et al. 2016), 3 –Albic Luvisols in the Tobolsk upland (Semenkov et al. 2019), 4 – Albic Retisols in the Central Forest Nature Reserve (Karavanova and Malinina 2009), 5 – Europe agricultural soils – GEMAS (Reimann et al. 2018), 6 – Regosols of the Smolensk-Moscow Upland (Samonova et al. 2018), 7 – soils of the Southern Russia (Dyachenko and Matasova 2016)**

The *Cv* of the content of the mobile fractions (F1, F2, F3) in the A-horizon of soils of the southern taiga catena are above 30% for all chemical elements, except for the F1 of Ni and F2 of Bi and Pb. The content of F1 of most elements is higher than in Albic Luvisols of the Tobolsk Upland (Table 2), where the gleying of the entire soil profile provides more favorable conditions for the removal of elements. The content of F3 of many studied elements in the A-horizon of studied Retisols is slightly lower than in Albic Luvisols of the Tobolsk Upland (Table 1), which is due to the lower degree of gleying of the studied soils. The F3 accounts for the major share of the total content of HMMs, which may indicate their high contribution to the physicochemical migration in Central Forest Nature Reserve soils and is typical for soils at the southern taiga (Semenkov et al. 2019).

## Mobility of chemical elements in the soil catena.

Extractability of HMMs (Table 1) which correlates with phytoavailability is the highest in the acidic O-horizon and lower in the subsoil horizons with the near-neutral environment (Fig. 4). The ratio of fractions depends on the properties of soil horizons and chemical elements. Among the mobile fractions of Co, Mn, Cd and Zn in the A-horizon, F2 and F3 account for practically the same proportion, which confirms their active participation in biogenic migration in the southern taiga landscapes of the Central Forest "Reserve". The biological cycle plays a greater role in the migration of Cd, Mn, Pb and Zn in the Central Forest Nature Reserve soils than for As, Bi, Cu, Fe and Ni, which is reflected in the increased proportion of exchangeable fractions (F1>10% of the total), the most readily available to plants from the A- and O-horizons of soils (Gabarrón et al. 2019; Li et al. 2017).

According to their mobility, the chemical elements are divided into 3 groups (Table 1). The first group (Sb, Mo, Cr and U) is characterized by relatively low mobility in the soils. Permanently low mobility of Sb in the vast majority of the samples is due to the presence of insoluble clay minerals (Bolan et al. 2022; Kabata-Pendias and Szteke 2015). Low mobility of Sb in soils is also associated with just slight involvement of its F1 compounds in the biological cycle by plants (Table A.1) and the removal of easily soluble compounds of the element within slightly acidic, close to neutral (pH = 5.2-6.8) surface waters of the Mezha River (Minaeva and Andreev 2008).

Elements of the second group (As, Bi, Zn, Fe, Cu and Ni) are the highly mobile in the A- and O-horizons sampled in the summit and footslope positions (>25%) while in other horizons they are moderately mobile (5-25%). This could be explained for Bi by the probable accumulation of dissolved organic matter in the soils of the lower part of the slope, because the element is captured in the organic-mineral forms (Kabata-Pendias and Szteke 2015). Mobile fractions of Zn enter the soil with plant litter of deciduous plants in

**Table. 1. Mobility of chemical elements in the soil catena, %**

| Horizons | Sb | Mo | Cr | U | As | Bi | Zn | Fe | Cu | Ni | Co | Pb | Mn | Cd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Summit | | | | | | | | | | | | | |
| A | 2,8 | 7 | 8 | 5 | 35 | 53 | 91 | 52 | 68 | 69 | 79 | 100 | 100 | 100 |
| E | 2 | 3,8 | 10 | 11 | 9 | 17 | 13 | 37 | 16 | 8 | 41 | 41 | 31 | 40 |
| Bt | 0,6 | 9 | 7 | 15 | 6 | 12 | 17 | 16 | 16 | 32 | 50 | 40 | 66 | 78 |
| C | 1,1 | 1,9 | 4,8 | 22 | 5 | 6 | 15 | 8 | 17 | 36 | 46 | 29 | 67 | 62 |
| | Backslope | | | | | | | | | | | | | |
| A | 3,6 | 7 | 6 | 3,8 | 25 | 42 | 91 | 56 | 61 | 23 | 81 | 100 | 100 | 100 |
| E | 6 | 7 | 8 | 8 | 8 | 18 | 19 | 39 | 21 | 12 | 33 | 58 | 60 | 54 |
| Bt | 1,1 | 10 | 8 | 11 | 6 | 11 | 11 | 18 | 18 | 21 | 42 | 38 | 44 | 49 |
| C | 2,5 | 9 | 6 | 16 | 7 | 11 | 16 | 14 | 18 | 40 | 60 | 50 | 73 | 81 |
| | Footslope | | | | | | | | | | | | | |
| H | 4,9 | 8 | 12 | 24 | 57 | 67 | 43 | 100 | 70 | 59 | 52 | 100 | 24 | 100 |
| E | 1,3 | 3,2 | 8 | 12 | 23 | 12 | 15 | 16 | 21 | 11 | 8 | 44 | 3,8 | 51 |
| Bt | 1,3 | 10 | 11 | 11 | 11 | 16 | 22 | 35 | 34 | 44 | 67 | 35 | 69 | 75 |
| C | 1,6 | 12 | 12 | 12 | 8 | 16 | 29 | 19 | 23 | 40 | 54 | 32 | 65 | 69 |
| | Toeslope | | | | | | | | | | | | | |
| H | 1,3 | 56 | 6 | 6 | 21 | 100 | 77 | 45 | 79 | 28 | 14 | 100 | 8 | 100 |
| E | 1,3 | 8 | 8 | 11 | 24 | 15 | 12 | 35 | 17 | 9 | 16 | 42 | 12 | 46 |
| Bt | 1,1 | 8 | 10 | 15 | 6 | 13 | 17 | 31 | 30 | 28 | 46 | 37 | 72 | 69 |
| C | 0,8 | 9 | 9 | 14 | 4,7 | 9 | 15 | 20 | 20 | 34 | 60 | 27 | 68 | 29 |

Color indicates mobility (%): <5 5-25 25-50 >50 the catena upper part (Enchilik et al. 2020). Fe, Cu and Ni are highly mobile in the (sub)surface soil horizons (A, H and E).

Elements of the third group (Co, Pb, Mn and Cd) are highly mobile (>25% in most horizons), which is explained by their active involvement in the biological cycle (Enchilik et al. 2020). Mn, as an essential element for plants, accumulates in the topsoil due to active plant uptake (Enchilik et al. 2020). Readily available to plants F3 compounds of Co (Kabata-Pendias and Szteke 2015) contribute a lot to the extractability of the metal in the A-horizon sampled in the summit and backslope positions (F3=36% and 41%, respectively). Pb forms complexes with soil organic matter (Fan et al. 2015). The maximum mobility of Mn and Pb was also found in other texture-differentiated soils (Semenkov et al. 2016). Cd becomes more soluble in the acidic humus horizon (Kabata-Pendias and Szteke 2015). Cd and Pb remain highly mobile in the E-horizon due to sorption by Mn (hydr)oxides (Violante 2013; Vodyanitskii 2010). Cd, Mn and Pb are highly mobile in the subsoil due to the vertical migration of dissolved organic matter (Fan et al. 2015).

## Vertical soil-geochemical structure of the catena

The vertical distribution of chemical elements is determined by geochemical barriers occurring in the soil horizons. Biogeochemical, sorption, gley and carbonate geochemical barriers were diagnosed in Retisols of the Central Forest Nature Reserve. The ability of chemical elements to accumulate at (no) one or several vertical geochemical barriers defines four types of vertical distribution.

*Accumulative distribution.* The total content of Bi and Cd are retained in the topsoils (Table A.3). The accumulation of HMMs in the O- and A-horizons is primarily due to the presence of a biogeochemical barrier. Topsoil accumulation of the total content of Cd (Fig. B.1a) is apparently due to the return of plant litter enriched with the element to the soil surface (Enchilik et al. 2020).

F1 compounds of As, Bi, Cd, Cr, Mn, Mo, Pb and Zn accumulate in the topsoil (Table A.4). There is a direct correlation of F1 of As, Bi, Cd, Cr, Mn, Mo, Pb and Zn (Fig. 6a, Fig. 7, Table A.3) with SOM content (Table A.5). Mn enters the soil surface in the backslope position with abundant plant remains – the fresh leaf litter horizon is thicker in this part of the catena (Enchilik et al. 2020). Exchangeable Mo is weakly mobile under acidic conditions and binds to SOM (Kabata-Pendias and Szteke 2015).

F2 compounds of Cd, Cr, Cu, Pb, Sb, Zn accumulate in the topsoil (Table A.4). The content of F2 compounds of Bi, Sb and essential Ni and Zn (Fig. 6b) correlates with SOM (Table A.5). The formation of Ni complexes with dissolved organic matter was pointed in (Semenkov et al. 2016; Avessalomova 2017). The O-horizon and especially peat are highly capable of absorbing the anionic Cr (Kyziol et al. 2006). Its association with humic substances is confirmed by high values of the stability constant with fulvic acids (Moiseenko et al. 2013).

The F3 fraction of Pb and Sb accumulates in the topsoil (Fig. B.1b). Anionic Sb accumulates in the A-horizon since it is weakly mobile in the acidic media (Manaka 2006), is sorbed by organic matter (Table A.5), and forms compounds with humic acids (Bolan et al. 2022). Vertical distribution of the total content and F3 compounds of HMMs shows in Annex (Fig. B.1).

*Accumulative-eluvial-illuvial distribution.* The total content of Sb increases at the biogeochemical barrier in the A-horizon (Fig. 7) as a part of insoluble humin. Correlation with SOM content (Table A.5) is positive for all fractions of the element. The total content of Sb is also higher in the Bt-horizon, which indicates its possible presence in poorly soluble primary clay minerals (Bolan et al. 2022; Kabata-Pendias and Szteke 2015). The complexes (F2) of Sb with organic matter are formed in the topsoil and with carbonates in the BCk-horizon. Zn accumulates at the sorption barrier in the Bt-horizon. F1 and F2 compounds of Ni accumulates in the waterlogged toeslope position due to the conservation of F1 compounds in the H-horizon, which is typical for such conditions (Semenkov et al. 2016; Avessalomova 2017). Its F1 fraction tends to accumulate at the alkaline geochemical barrier (Table A.5, Fig. 7). The content of F3 fraction of Pb correlates with the content of SOM, and that of Cu and Zn with clay particles (Table A.5, Fig. 7).

*Eluvial distribution.* Slightly mobile As under acidic conditions could be sorbed by iron nodules accumulated in the lower part of the E-horizon (Lee et al. 2011; Vodyanitskii 2010). The content of Cu increases in the subsoil (Table A.5) due to its accumulation at alkaline and sorption geochemical barriers (Boyd 2020; Kabata-Pendias and Szteke 2015). The Zn content in the slope soils increases under alkaline conditions in the parent rocks due to the increase in carbonates.

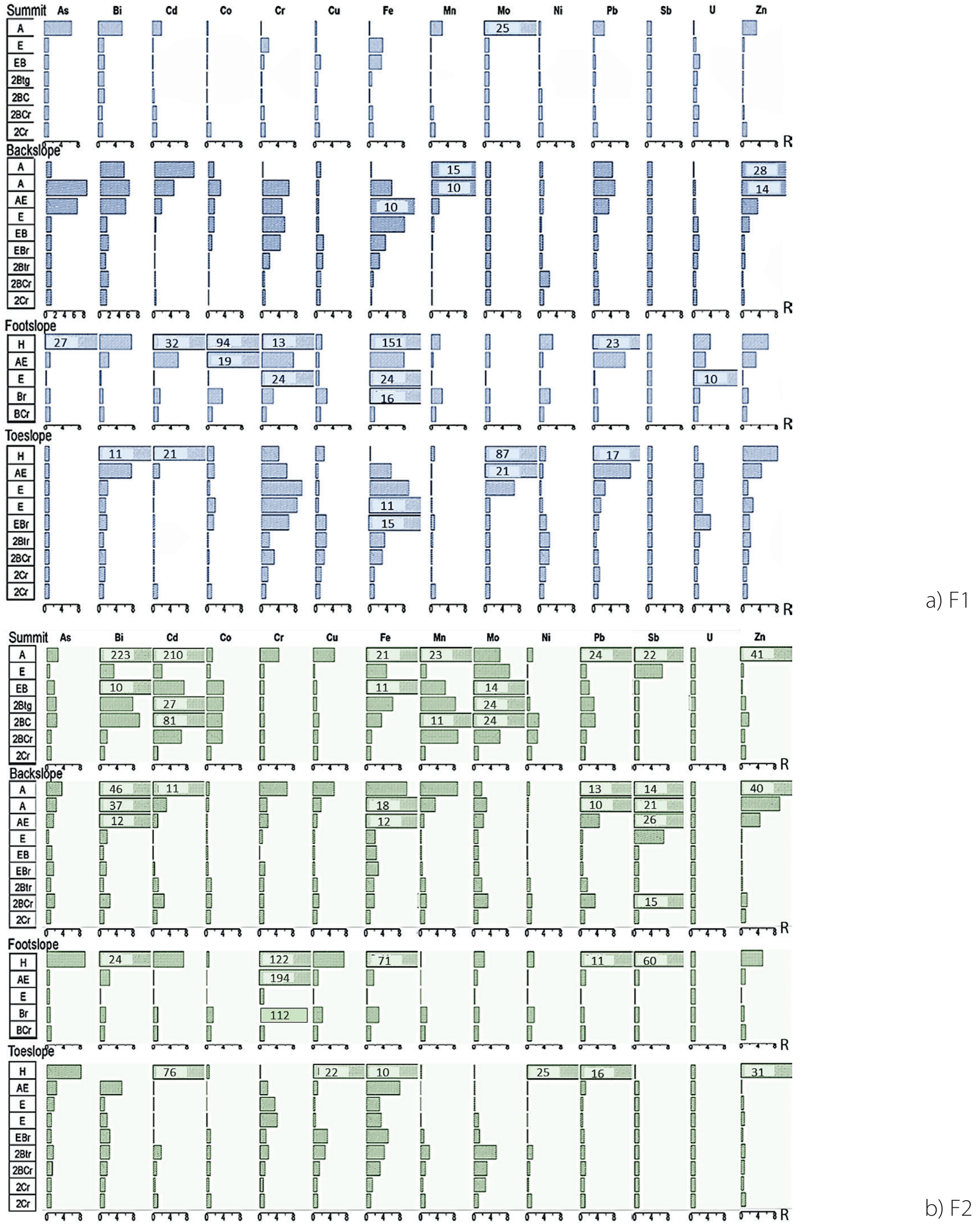
The content of the F1 fraction of Fe in the summit Retisols and Ni in the slope Retisols increases in the middle part of the soil profile (Table A.4). Exchangeable Cu accumulates at the alkaline geochemical barrier in the subsoil (Table A.4, Fig. 7).

The F2 fraction of Fe accumulates in the Bt-horizon which confirms its ability to form compounds with carbonates (Thompson et al. 2006). Accumulation in the middle part of the Retisols is characteristic of the F2 fraction of Cu due to the migration of its organic complexes (Kabata-Pendias and Szteke 2015; Moiseenko et al. 2013).

High content of the F3 fraction of Fe and Cr is observed in the E-horizon due to their accumulation in abundant ferruginous nodules (Vodyanitskii 2010) and in the BCk-horizon at the alkaline geochemical barrier (Table A.4). The F3 fraction of As, Bi, Cd, Pb accumulates in the middle part of the Retisols due to the abundance of Fe–Mn nodules in the horizons (Lee et al. 2011; Violante 2013). As is absorbed with iron (hydr)oxides. And Cd and Pb are absorbed with manganese (hydr)oxides (Vodyanitskii 2010). Accumulation of Cu in the middle part of the Retisols seemed to result from the influence of the manganese (hydr)oxides, too (Perelomov and Chulin 2014). Bi leaches out from the A-horizon and accumulates in the middle part of the Retisols due to the adsorption by clay (Pasieczna 2012). Cr and U accumulate in the lower part of the Retisols, since the distribution of these elements is related to the eluvial-illuvial distribution of clay particles (Table A.5, Fig. 7).

*The ground-accumulative distribution* is characteristic of total Bi, Cd, Ni, Pb and Sb, exchangeable Co, Ni, and U, F2 of Co, Mn and Mo, and F3 of Bi, Co, Cr, Fe, Mn and Ni. The concentration of exchangeable Ni and Cu correlates with the distribution of clay (Table A.4, A.5, Fig. 7). Complexes of Mn are carried out to the parent rocks in the waterlogged toeslope position.

F1 of As, Bi, Cd, Cr, Mn and Pb and F3 of Pb and Sb accumulate at the biogeochemical barrier (Fig. 7, Table A.5) of soils studied due to sorption by organic matter. Formation of organic complexes with As, Bi, Cr and Zn might be the reason for a positive correlation between the content of F2 fraction of these elements and SOM (Table A.5). The accumulative-eluvial-illuvial distribution of the total content of Sb and Zn, F2 of Fe and F3 of Cu, Pb and Zn depends on the content of soil organic matter and clay. The eluvial distribution of the total content of As, Co, Cu and Cr, F1 of Cu and F3 of Cr is governed by clay and co-precipitation with carbonates (Table A.5). The ground-accumulative distribution is determined by the accumulation of compounds with fine particles and with carbonates and hydroxides at the alkaline barrier in the subsoil horizons (Table A.5).



a) F1

b) F2

Fig. 6. The vertical differentiation (R) of the F1 (a) and the F2 (b) fraction of the HMMs in the soil catena studied

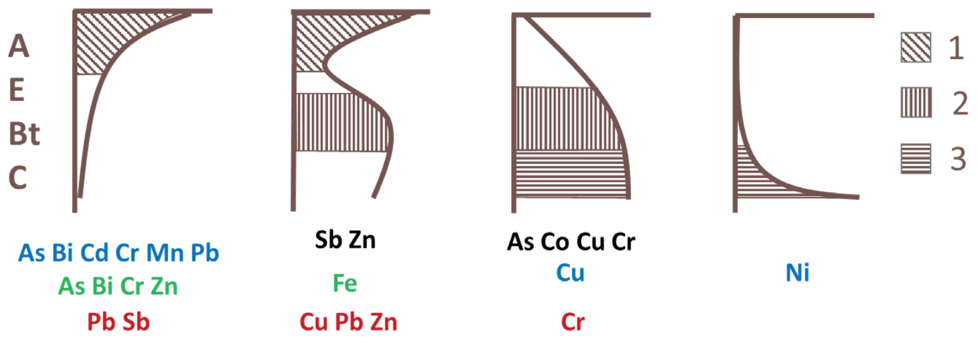


Fig. 7. Accumulation sites of HMMs at the barriers in the soil horizons sampled in the catena located in the Central Forest Nature Reserve. The colors indicate the forms of chemical elements: black – total content, blue – F1, green – F2, red – F3. Geochemical barriers: 1 – biogeochemical, 2 – sorption, 3 – alkaline. The presented elements have the same type of vertical distribution in soils of two or more positions and accumulate on geochemical barriers, confirmed by correlation coefficients (Table A.4)

## Spatial soil-geochemical structure of the catena

The intensity of lateral flows of chemical elements depends on the migrational contrasts (Perel'man 1967). The most considerable role in the distribution of HMMs in forest soils is played by the spatial sorption-biogeochemical barrier. Therefore, two variants of the contrasting distribution of elements in the studied catena within the Central Forest Nature Reserve were identified depending on the location of the barrier.

*Accumulation in the backslope position.* In the backslope position, HMMs mainly accumulate at the biogeochemical barrier. Here the biomass reaches its maximum and the abundant leaf litter enriched with Cd, Zn, Mn, and Ni enters the soil surface (Enchilik et al. 2020). The total content of Bi, Cd, Pb, Sb and Zn is maximal in the A-horizon, too. Total As, Mn and Ni accumulate to a greater degree in the A-horizon sampled in the backslope position (Fig. B.2a).

F1 fractions of Zn accumulates in the A-horizon in the backslope position (Fig. 8a, Fig. 9) due to the transformation of plant litter (Enchilik et al. 2020, Table A.4).

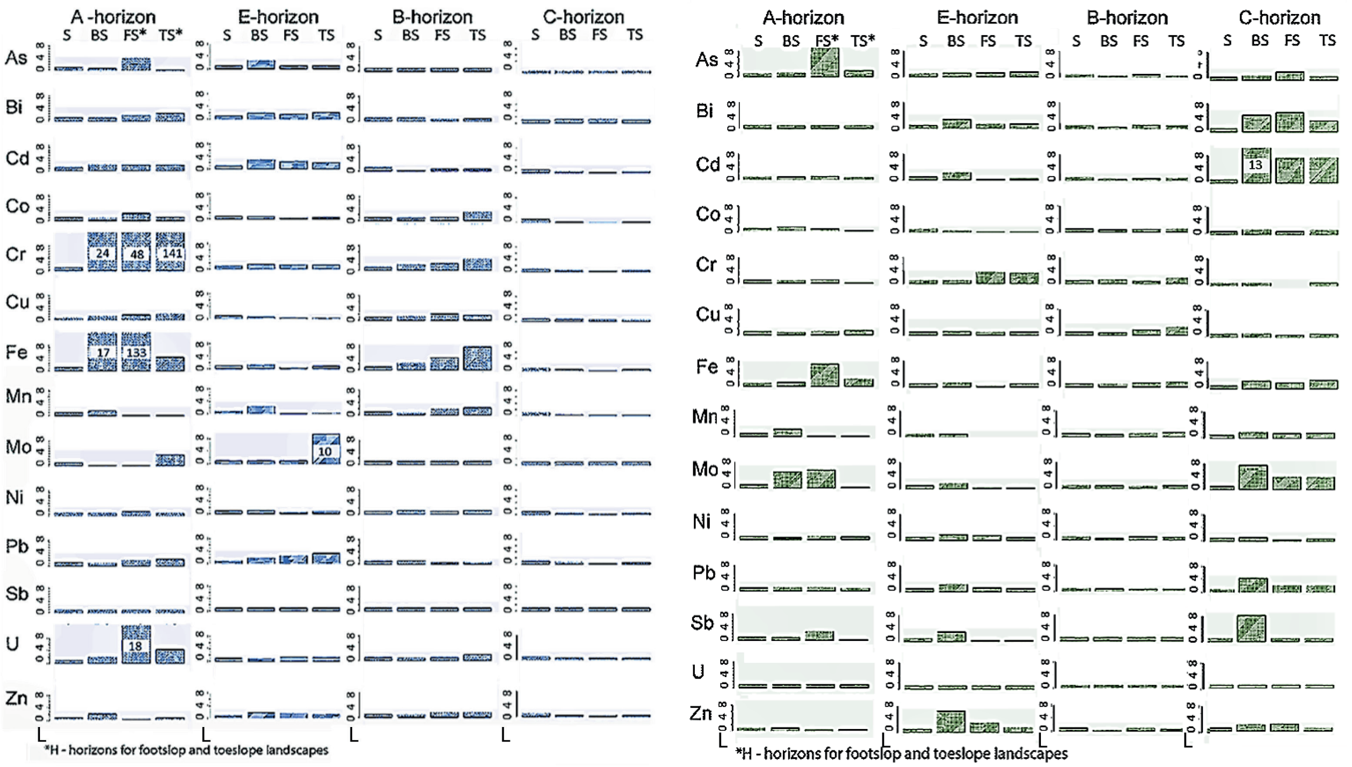
The content of exchangeable compounds of Mn is maximal (Fig. 9) in the E-horizon sampled in the backslope position.

F2 of Mo accumulates (Fig. 8b) in the A-horizon sampled in the backslope position. F2 of Bi, Cd, Pb and Sb accumulates (Fig. 9) in the E-horizon. Slope soils tend to accumulate F3 of As at the spatial geochemical barrier in the A-horizon (Fig. B.2b), Sb at the eluvial and As again at the E-horizon. Spatial distribution of the total content and F3 fraction is given in the Annex (Fig. B.1).

*Accumulation in the footslope and toeslope positions.* The migration slows down in the toeslope positions of the catena. And the total content of many HMMs increases at the spatial geochemical barrier of peaty soils (Fig. B.2a). The role of oxidative and reductive barriers in the E-horizon increases in this position. The total content of As in the A-horizon is maximal in the soils sampled at the footslope position probably due to the accumulation of humic substances washed away from the summit position. Peat of the toeslope position is enriched in Fe which accumulates in sphagnum more actively than other elements (Enchilik et al. 2020), and depleted in Mo due to its lower phytoavailability in acidic Fe-saturated soils (Kabata-Pendias and Szteke 2015).

The content of F1 of As, Bi, Cr, Fe, Mo and U in the O-horizon increases down the catena (Fig. 8a). The spatial geochemical barrier in peaty soils at the toeslope positions was previously reported in the taiga catenas (Avessalomova 2017; Semenkov et al. 2019; Semenkov et al. 2016). F1 of Mo is absorbed by Fe-Mn nodules in the E-horizon sampled at the toeslope position. The content of Bi, Cd and Pb in the E-horizon increases when moving down the catena. F1 of Co, Cr, Fe and Mn in the Bt-horizon also accumulates in the lower part of the catena (Fig.9).

F2 of As, Fe, Mo and Sb accumulates at the spatial biogeochemical barrier in the H-horizon of the toeslope position (Fig. 8b) due to migration of organic compounds from the upper-situated landscapes. The distribution of As is associated with soil organic matter (Table A.4). Fe compounds with high stability constants with humic acids (Moiseenko et al. 2013) actively migrate downslope with surface runoff under the acidic conditions and accumulate in the soils of the lower catena part. F2 of anionic Cr accumulates in the E-horizon sampled in the footslope and toeslope positions probably due to the slower migration of the element under strongly acidic conditions (pH=3.7 and 3.9, respectively, Fig. 4). F2 of Bi, Cd, Mo, Sb and Zn accumulates in the C-horizon of the footslope position (Fig. 9), which could be provoked by frequent changes in redox conditions near shallow groundwater table (Fig. 3) and the formation of complex oxygen and gley barriers. F3 of Fe accumulates in the H-horizon sampled in the footslope position (Fig. B.2b), As in the Bt-horizon, and Mo in the Ck-horizon (Fig. 9).


a) F1

b) F2

**Fig. 8. The spatial differentiation (L) of the F1 (a) and the F2 (b) fraction of the HMMs in the soil catena studied**

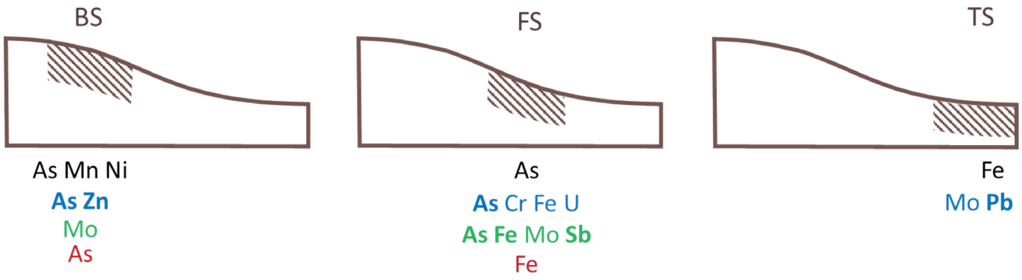


**Fig. 9. Accumulation sites of HMMs at the lateral biogeochemical barrier in catena soils (hatching): BS– backslope, FS – footslope, TS – toeslope. The colors indicate the forms of chemical elements: black – total content, blue – F1, green – F2, red – F3. Bold (italic) - accumulation of elements at geochemical barriers is confirmed by correlation with soil properties (Table A.5).**

The contrast of spatial differentiation of elements generally decreases along A–E–Bt–Ck series of horizons, which is due to the lithogeochemical homogeneity of the catena and weakening of the influence of the heterogeneity of the vegetation cover in the underlying soil horizons. The exchangeable and complex compounds of many elements accumulate on the biogeochemical barrier of peaty soils of the foot slope position (Fig. 9), which is confirmed by positive correlation with SOM (Table A.5) for F1 of As and F2 of As, Fe and Sb. The exchangeable fraction total content of Zn increases at the biogeochemical barrier of soils sampled at the backslope position due to the transformation of plant litter (Enchilik et al. 2020).

## CONCLUSIONS

The studied background Retisols and Stagnosols of the southern taiga catena at the Central Forest Nature Reserve have relatively high content of F1 of most of the studied elements in the acid A-horizons.

The high content of the F1 in the E- and Bt-horizons is due to the change in redox conditions and the increase of pH values in the parent rocks. The leaching water regime results in the lower content of F3 fraction of HMMs in the A-, H- and O-horizons. HMMs accumulated in Fe-Mn nodules in the E-horizon. The variability of the total content of elements in the A-horizon is within the range of 20-75%. The F1 fraction of Mo, Fe, As, U and Cr, F2 of As, Mn and Fe, and F3 of Bi, Sb, and Mn show the highest variability in the horizon.

The highest *extractability* of elements is characteristic of organic horizons, where the share of F2 and F3 fractions is practically the same. The proportion of the F1 fraction in the A-horizon is maximum for Cd, Mn, Pb and Zn. Cd, Co, Pb, and Mn are highly mobile.

The extractability decreases significantly towards the underlying subsoil horizons. Both Cd and Pb are highly mobile (40-58%) in the E-horizon of all soils. Mobility of As, Bi, Zn, Fe, Cu. Ni and Co decreases to 8%. Only Cd, Pb, and Mn are mobile (>25%) in the Bt- and C-horizons.

The *vertical* distribution of F1 of elements depends considerably on biogeochemical processes (absorption by plants from subsoil horizons, return with litter to the soil surface, humus accumulation) and sorption by soil organic matter. The key factors of F2 distribution are the content of SOM and carbonates. As, Cd, Cu, Pb, Zn and Sb accumulated on the biogeochemical barrier in the A-horizon. As, Bi, Cd and Pb accumulated on the sorption barrier of Fe-Mn nodules in the E- and Bt-horizons. Migration with silt is important for the distribution of F3 fraction of Cr and U. The biological cycle plays the greatest role in the migration of highly-mobile Cd, Mn and Pb in soils of the catena, since their F1 are observed to accumulate in the topsoil.

The *spatial* distribution of the total content of Bi, Cd, Pb, Sb and Zn, F1 of Zn, F2 of Mo and F3 of As, Fe and Bi depends on the biological cycle in the backslope landscape. Here, the abundant leaf litter enriched with HMMs mobile fraction enters the soil surface. Mobile forms of As, Mo and Sb (F2), and Fe (F2, F3) accumulated at the spatial biogeochemical barrier in the H-horizon sampled at the footslope position due to the accumulation of humic substances washed off from summit positions. Fe and the most mobile (F1) fraction of As, Bi, Cr, Fe, Mo, Pb and U accumulate on the spatial geochemical barrier of peat soils in the lower part of the catena. This process indicated the ability of peat to conserve the most biologically available F1 fractions of both mobile Pb, Fe, Bi and As and less mobile U, Cr and Mo.

Thus, both total content and the concentration of F3 of elements increases in the A-horizon of the slope soils, and F2 in the H-horizon of the footslope position, while the peat of the waterlogged toeslope position entraps F1. The contrast of spatial differentiation of the mobile fractions decreases from the topsoil horizons to the parent material, which is mainly due to the smaller effect of vegetation cover and biological factor on deep soil horizons.

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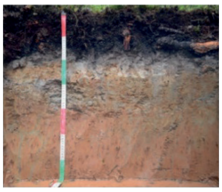
## APPENDICES

### Table A.1. Morphological properties of the studied soils

| Position | Photos of soil pits | Soils and horizons (Barham et al., 2006; IUSS Working Group WRB, 2014) | | Coordinates of soil pits | Plant dominants | | |
|---|---|---|---|---|---|---|---|
| | | | | | Trees | Shrubs | Herbs and mosses |
| Summit |  | Endocalcaric Albic Neocambic Stagnic Glossic Retisols (Geoabruptic, Chromic, Loamic) | Oi–Oe–Oa–OAh–E–BE–2Btk–2BClk | N56°27′48.7″ E32°57′45″ | *Picea abies, Tilia cordata, Acer platanoides, Ulmus glabra* | *Corylus avellana* | *Stellaria holostea, Anemone nemorosa, Lamium galeobdolon, Oxalis acetosella, Pteridium aquilinum, Aegopodium podagraria* |
| Backslope |  | Endocalcaric Albic Neocambic Stagnic Glossic Retisols (Geoabruptic, Lamellic, Loamic, Ochric) | Oi–Oe–Oa–OAh–Ah–AhE–Escl–BEscl–Bescl–2Btsc–2CBwsc | N56°27′47.5″ E32°56′15.4″ | *Picea abies, Tilia cordata, Acer platanoides* | *Corylus avellana, Sorbus aucuparia, Lonicera xylosteum* | *Hepatica nobilis, Galium odoratum, Pteridium aquilinum, Lamium galeobdolon, Asarum europaeum, Equisetum sylvaticum, Pulmonaria obscúra, Anemone nemorosa, Stellaria holostea, Oxalis acetosella* |
| Footslope |  | Endocalcaric Glossic Albic Gleyic Histic Stagnosols (Geoabruptic, Loamic) | Oi–Oe–Ha–Ah–AhEl–Etosc–Btg | N56°27′47.1″ E32°56′19.8″ | *Picea abies, Tilia cordata, Acer platanoides* | *Sorbus aucuparia* | *Vaccinium myrtillus* |
| Toeslope |  | Endocalcaric Glossic Albic Histic Stagnosols (Geoabruptic, Loamic) | Oi–Oe–Ha–HaE–Eoscl–Eoscl–BEtoscl–Bg–2Crk | N56°27′48.0″ E32°56′21.1″ | *Picea abies, Tilia cordata, Acer platanoides, Salix caprea* | *Sorbus aucuparia* | *Pteridium aquilinum, Oxalis acetosella, Vaccinium myrtillus, Sphagnum* |

### Table A2. Physicochemical properties of Retisols studied

| Granulometric fractions (µm) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Position | Horizons | Sampling depth, cm | 500–1000 | 250–500 | 50–250 | 10–50 | 5–10 | 1–5 | <1 | pH | $CaCO_3$,% | TOC, % |
| Summit | OAh | 2-6 | 0 | 0 | 15 | 58 | 13 | 13 | 2 | 4.8 | na | 31 |
| | E | 20-30 | 0 | 0 | 19 | 59 | 8 | 11 | 2 | 4.9 | na | 0.3 |
| | BE | 45-55 | 0 | 0 | 18 | 60 | 6 | 11 | 5 | 4.6 | na | 0.32 |
| | 2Btk | 70-90 | 0 | 0.2 | 17 | 38 | 13 | 25 | 6 | 5.1 | na | 0.12 |
| | 2BCk | 110-130 | 0 | 0 | 14 | 36 | 15 | 27 | 8 | 6.7 | na | 0.10 |
| | 2BClk | 150-170 | 0 | 0 | 18 | 35 | 14 | 25 | 8 | 7.5 | 7.8 | 0.10 |
| | 2Clk | 200 | 0 | 0.3 | 16 | 36 | 14 | 25 | 9 | 7.5 | 10.4 | 0.17 |
| Backslope | OAh | 2,5-4 | 0 | 0 | 5 | 66 | 13 | 14 | 3 | 5.0 | na | 18 |
| | Ah | 5-10 | 0 | 0 | 4 | 67 | 13 | 14 | 3 | 4.5 | na | 7.19 |
| | AhE | 12-18 | 0 | 0 | 1 | 61 | 16 | 18 | 4 | 4.0 | na | 3.60 |
| | E | 30-40 | 0 | 0 | 10 | 60 | 10 | 15 | 4 | 4.5 | na | 0.55 |
| | EB | 52-62 | 0 | 0 | 18 | 59 | 7 | 12 | 4 | 4.7 | na | 1.62 |
| | EB | 75-85 | 0 | 0 | 28 | 56 | 5 | 8 | 3 | 5.4 | na | 0.19 |
| | 2Btl | 104-114 | 0 | 0 | 19 | 37 | 12 | 25 | 7 | 5.5 | na | 0.14 |
| | 2BCl | 140-150 | 0 | 0.1 | 24 | 34 | 12 | 23 | 7 | 6.5 | na | 0.20 |
| | 2Cl | 200 | 0 | 0.03 | 19 | 36 | 13 | 24 | 7 | 7.3 | 4.8 | 0.13 |
| Footslope | Ah | 9-14 | na | na | na | na | na | na | na | 4.8 | na | 28 |
| | AhE | 17-20 | 0 | 2.4 | 36 | 45 | 7 | 8 | 2 | 3.7 | na | 5.74 |
| | E | 25-35 | 0 | 0 | 16 | 60 | 9 | 12 | 3 | 4.4 | na | 1.19 |
| | Btg | 48-58 | 0 | 0 | 33 | 49 | 5 | 10 | 3 | 6.1 | na | 0.14 |
| | BCl | 100 | 0 | 0 | 22 | 63 | 5 | 7 | 3 | 6.4 | na | 0.04 |
| Toeslope | Ha | 0-8 | na | na | na | na | na | na | na | 4.0 | na | 3.41 |
| | HaE | 8-12 | 0 | 1.9 | 34 | 48 | 7 | 8 | 2 | 3.8 | na | 4.65 |
| | E | 17-23 | 0 | 0 | 15 | 61 | 10 | 12 | 3 | 3.9 | na | 1.10 |
| | E | 28-35 | 0 | 0 | 12 | 62 | 9 | 13 | 3 | 4.7 | na | 0.48 |
| | BEl | 39-45 | 0 | 0 | 14 | 60 | 8 | 13 | 4 | 4.9 | na | 0.25 |
| | 2Bl | 60-70 | 0 | 0 | 23 | 59 | 6 | 9 | 3 | 5.3 | na | 0.07 |
| | 2BClk | 80-90 | 0 | 0 | 17 | 61 | 7 | 12 | 3 | 5.6 | na | 0.11 |
| | 2Clk | 110-120 | 0 | 0 | 21 | 36 | 13 | 25 | 5 | 5.7 | na | 0.15 |
| | 2Clk | 200 | 0 | 0.2 | 18 | 34 | 14 | 27 | 7 | 7.5 | 3.0 | 0.15 |

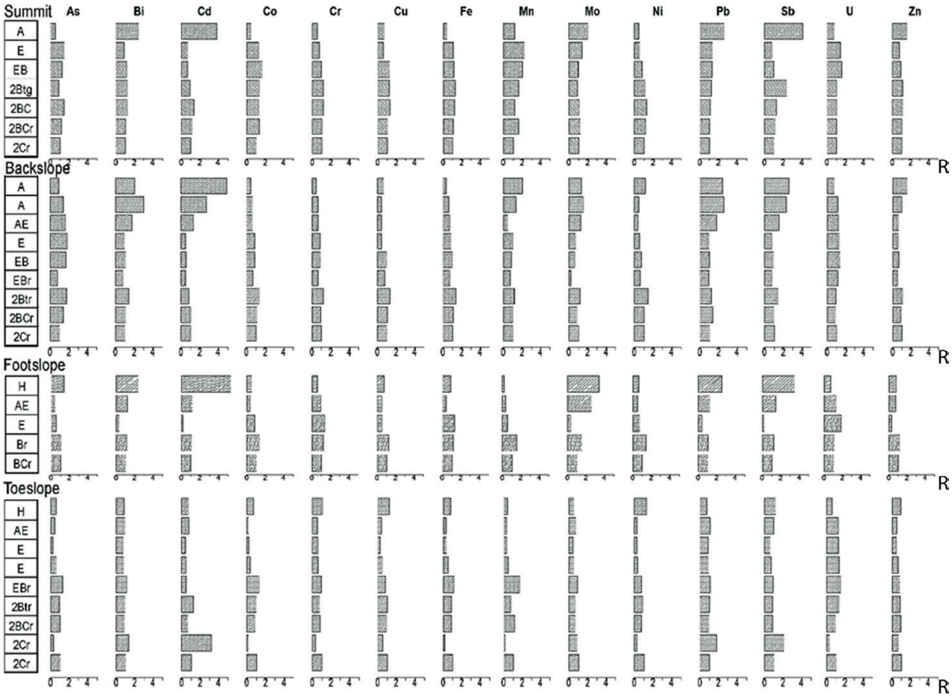
**Table A3. Content of HMMs in the Retisols studied**

| Position | Horizons | Sampling depth, cm | As | Bi | Cd | Co | Cr | Cu | Fe | Mn | Mo | Ni | Pb | Sb | U | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Total content | | | | | | | | | | | | | | | | |
| Summit | OAh | 2-6 | 1.4 | 0.37 | 0.69 | 3.4 | 20 | 12 | 4700 | 600 | 0.80 | 9 | 34 | 1.10 | 1.3 | 91 |
| | E | 20-30 | 3.8 | 0.13 | 0.12 | 9.2 | 29 | 10 | 13800 | 1100 | 0.56 | 11 | 18 | 0.20 | 2.4 | 43 |
| | BE | 45-55 | 3.1 | 0.17 | 0.11 | 12.4 | 38 | 22 | 15000 | 1000 | 0.40 | 17 | 17 | 0.26 | 2.6 | 50 |
| | 2Btk | 70-90 | 2.3 | 0.18 | 0.16 | 10.2 | 47 | 21 | 16200 | 800 | 0.37 | 22 | 16 | 0.64 | 1.8 | 66 |
| | 2BCk | 110-130 | 3.7 | 0.18 | 0.24 | 9.1 | 47 | 22 | 15900 | 600 | 0.43 | 26 | 15 | 0.34 | 1.8 | 67 |
| | 2BClk | 150-170 | 3.0 | 0.15 | 0.21 | 10.1 | 41 | 18 | 14100 | 800 | 0.49 | 24 | 14 | 0.31 | 1.7 | 59 |
| | 2Clk | 200 | 2.6 | 0.15 | 0.18 | 7.5 | 41 | 17 | 12900 | 500 | 0.41 | 20 | 13 | 0.27 | 1.7 | 58 |
| Backslope | OAh | 2,5-4 | 1.7 | 0.28 | 0.98 | 3.8 | 19 | 12 | 3800 | 1400 | 0.58 | 23 | 35 | 0.69 | 1.3 | 112 |
| | Ah | 5-10 | 2.5 | 0.42 | 0.54 | 5.1 | 29 | 7 | 8300 | 900 | 0.66 | 9 | 36 | 0.62 | 2.0 | 70 |
| | AhE | 12-18 | 3.0 | 0.24 | 0.26 | 5.1 | 29 | 7 | 9600 | 300 | 0.55 | 8 | 25 | 0.41 | 2.1 | 45 |
| | E | 30-40 | 3.3 | 0.13 | 0.09 | 7.3 | 37 | 7 | 10800 | 700 | 0.33 | 10 | 14 | 0.19 | 2.2 | 39 |
| | EB | 52-62 | 3.0 | 0.15 | 0.11 | 7.3 | 38 | 17 | 12900 | 600 | 0.26 | 15 | 14 | 0.24 | 2.4 | 47 |
| | El | 75-85 | 1.5 | 0.11 | 0.10 | 5.6 | 28 | 14 | 9700 | 500 | 0.09 | 12 | 13 | 0.19 | 2.0 | 36 |
| | 2Btl | 104-114 | 3.1 | 0.19 | 0.16 | 10.8 | 52 | 23 | 17500 | 800 | 0.52 | 29 | 17 | 0.38 | 1.6 | 78 |
| | 2BCl | 140-150 | 2.6 | 0.15 | 0.20 | 9.2 | 40 | 19 | 14400 | 700 | 0.39 | 21 | 19 | 0.26 | 1.5 | 63 |
| | 2Cl | 200 | 1.8 | 0.14 | 0.20 | 8.3 | 44 | 18 | 13200 | 700 | 0.45 | 21 | 14 | 0.27 | 1.8 | 73 |
| Footslope | Ah | 9-14 | 3.5 | 0.26 | 0.64 | 3.1 | 17 | 10 | 8700 | 100 | 0.61 | 7 | 33 | 0.66 | 1.2 | 29 |
| | AhE | 17-20 | 1.0 | 0.13 | 0.14 | 2.0 | 27 | 6 | 3900 | 200 | 0.46 | 6 | 16 | 0.27 | 2.3 | 25 |
| | E | 25-35 | 0.7 | 0.11 | 0.08 | 2.8 | 28 | 6 | 6300 | 300 | 0.25 | 7 | 13 | 0.20 | 2.4 | 25 |
| | Btg | 48-58 | 2.7 | 0.12 | 0.13 | 8.2 | 33 | 16 | 11800 | 900 | 0.27 | 17 | 14 | 0.23 | 1.9 | 41 |
| | BCl | 100 | 2.5 | 0.11 | 0.12 | 6.3 | 28 | 13 | 10100 | 600 | 0.18 | 12 | 13 | 0.19 | 1.8 | 36 |
| Toeslope | Ha | 0-8 | 2.1 | 0.11 | 0.09 | 5.9 | 32 | 13 | 10600 | 400 | 0.27 | 14 | 13 | 0.23 | 1.3 | 39 |
| | HaE | 8-12 | 1.2 | 0.14 | 0.14 | 1.8 | 26 | 7 | 4400 | 200 | 0.36 | 5 | 16 | 0.30 | 2.3 | 29 |
| | E | 17-23 | 0.6 | 0.11 | 0.08 | 2.0 | 27 | 4 | 4500 | 200 | 0.21 | 5 | 13 | 0.18 | 2.3 | 24 |
| | E | 28-35 | 1.7 | 0.12 | 0.09 | 3.5 | 30 | 10 | 7300 | 300 | 0.24 | 8 | 14 | 0.22 | 2.4 | 36 |
| | BEl | 39-45 | 3.8 | 0.16 | 0.09 | 13.4 | 44 | 16 | 17700 | 1200 | 0.44 | 18 | 16 | 0.28 | 2.7 | 43 |
| | 2Bl | 60-70 | 2.6 | 0.14 | 0.23 | 10.4 | 35 | 20 | 12900 | 500 | 0.32 | 21 | 15 | 0.26 | 2.4 | 46 |
| | 2BClk | 80-90 | 2.9 | 0.13 | 0.12 | 9.0 | 37 | 18 | 13300 | 800 | 0.31 | 19 | 14 | 0.26 | 1.6 | 50 |
| | 2Clk | 110-120 | 0.8 | 0.20 | 0.61 | 1.6 | 15 | 10 | 2600 | 100 | 0.43 | 6 | 27 | 0.64 | 0.6 | 38 |
| | 2Clk | 200 | 2.9 | 0.15 | 0.19 | 10.6 | 46 | 20 | 15700 | 700 | 0.51 | 24 | 15 | 0.31 | 1.8 | 55 |
| Exchangeable compounds (F1) | | | | | | | | | | | | | | | | |
| Summit | OAh | 2-6 | 0.05 | 0.019 | 0.20 | 0.27 | 0.01 | 0.17 | 8 | 577 | 0.042 | 0.50 | 3.40 | <0.001 | 0.02 | 9.7 |
| | E | 20-30 | <0.01 | 0.004 | 0.02 | 0.20 | 0.45 | 0.19 | 284 | 27 | <0.002 | 0.27 | 0.41 | <0.001 | 0.08 | 1.15 |
| | BE | 45-55 | <0.01 | 0.005 | 0.01 | 0.14 | 0.17 | 0.75 | 262 | 17 | <0.002 | 0.27 | 0.65 | <0.001 | 0.19 | 0.75 |
| | 2Bwk | 70-90 | <0.01 | 0.004 | 0.01 | 0.03 | 0.06 | 0.40 | 54 | 12 | <0.002 | 0.32 | 0.65 | <0.001 | 0.12 | 0.65 |
| | 2BCk | 110-130 | <0.01 | 0.005 | 0.04 | 0.01 | 0.06 | 0.19 | 9 | 8 | <0.002 | 0.75 | 0.31 | <0.001 | 0.10 | 0.32 |

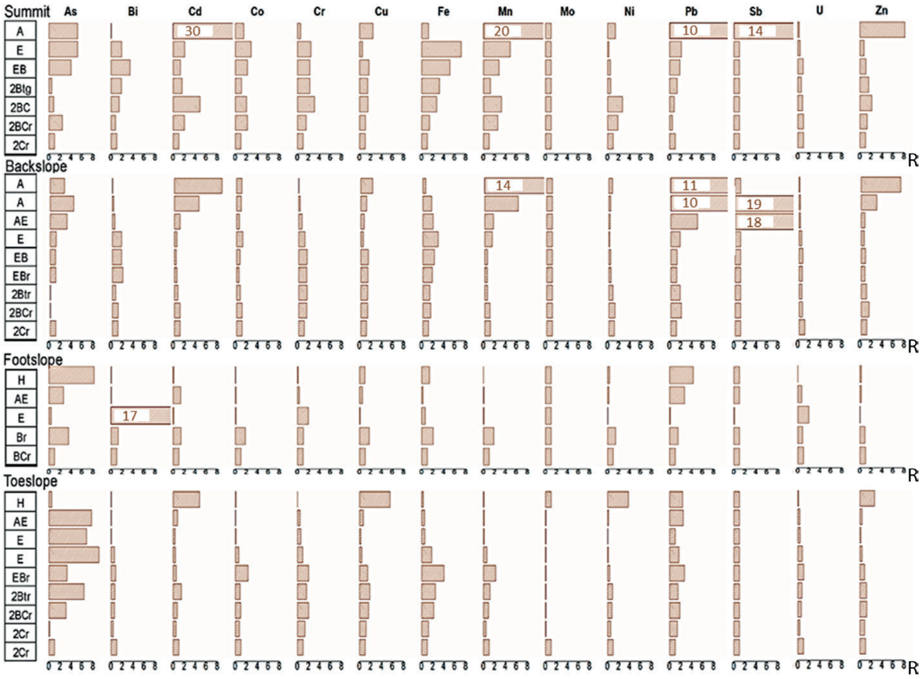
| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Summit | 2BClk | 150-170 | <0.01 | 0.003 | 0.09 | 0.25 | 0.19 | 0.41 | 72 | 137 | <0.002 | 0.85 | 0.65 | <0.001 | 0.17 | 0.95 |
| | 2Clk | 200 | <0.01 | 0.003 | 0.10 | 1.00 | 0.25 | 0.60 | 90 | 212 | <0.002 | 1.15 | 1.30 | <0.001 | 0.14 | 2.95 |
| Backslope | OAh | 2,5-4 | <0.01 | 0.015 | 0.53 | 0.15 | 0.01 | 0.29 | 11 | 1141 | <0.002 | 0.31 | 2.50 | <0.001 | 0.02 | 27.5 |
| | Ah | 5-10 | 0.07 | 0.019 | 0.26 | 0.33 | 0.60 | 0.18 | 266 | 787 | <0.002 | 0.43 | 2.85 | <0.001 | 0.04 | 14.0 |
| | AhE | 12-18 | 0.05 | 0.016 | 0.10 | 0.16 | 0.45 | 0.14 | 577 | 113 | <0.002 | 0.37 | 2.00 | <0.001 | 0.06 | 3.25 |
| | E | 30-40 | <0.01 | 0.004 | 0.02 | 0.16 | 0.50 | 0.15 | 427 | 35 | <0.002 | 0.17 | 0.40 | <0.001 | 0.11 | 1.48 |
| | EB | 52-62 | <0.01 | 0.005 | 0.01 | 0.09 | 0.41 | 0.50 | 188 | 13 | <0.002 | 0.32 | 0.60 | <0.001 | 0.14 | 0.50 |
| | El | 75-85 | <0.01 | 0.003 | 0.01 | 0.02 | 0.16 | 0.45 | 111 | 5 | <0.002 | 0.25 | 0.37 | <0.001 | 0.11 | 0.60 |
| | 2Btl | 104-114 | <0.01 | 0.005 | 0.01 | 0.01 | 0.05 | 0.32 | 32 | 6 | <0.002 | 1.00 | 0.60 | <0.001 | 0.06 | 0.25 |
| | 2BCl | 140-150 | <0.01 | 0.004 | 0.02 | 0.01 | 0.06 | 0.26 | 16 | 8 | <0.002 | 0.42 | 0.70 | <0.001 | 0.09 | 0.47 |
| | 2Cl | 200 | <0.01 | 0.003 | 0.07 | 0.13 | 0.11 | 0.36 | 61 | 75 | <0.002 | 0.50 | 0.65 | <0.001 | 0.12 | 1.00 |
| Footslope | Ah | 9-14 | 0.21 | 0.029 | 0.34 | 0.64 | 0.62 | 0.31 | 1114 | 15 | <0.002 | 0.64 | 6.10 | <0.001 | 0.29 | 3.60 |
| | AhE | 17-20 | <0.01 | 0.008 | 0.06 | 0.13 | 0.35 | 0.16 | 58 | 3 | <0.002 | 0.16 | 1.95 | <0.001 | 0.21 | 1.90 |
| | E | 25-35 | <0.01 | 0.005 | 0.01 | 0.04 | 0.50 | 0.11 | 201 | 2 | <0.002 | 0.11 | 0.80 | <0.001 | 0.17 | 1.15 |
| | Bwg | 48-58 | <0.01 | 0.003 | 0.02 | 0.02 | 0.13 | 0.60 | 124 | 19 | <0.002 | 0.50 | 0.25 | <0.001 | 0.11 | 0.80 |
| | BCl | 100 | <0.01 | 0.004 | 0.01 | 0.01 | 0.05 | 0.24 | 7 | 8 | <0.002 | 0.21 | 0.27 | <0.001 | 0.08 | 0.60 |
| Toeslope | Ha | 0-8 | <0.01 | 0.043 | 0.35 | 0.30 | 1.84 | 0.37 | 36 | 20 | 0.147 | 0.37 | 7.01 | <0.001 | 0.07 | 9.35 |
| | HaE | 8-12 | <0.01 | 0.018 | 0.07 | 0.11 | 0.30 | 0.11 | 129 | 4 | 0.036 | 0.24 | 3.46 | <0.001 | 0.17 | 2.11 |
| | E | 17-23 | <0.01 | 0.005 | 0.01 | 0.04 | 0.48 | 0.15 | 236 | 2 | 0.012 | 0.11 | 1.05 | <0.001 | 0.16 | 0.55 |
| | E | 28-35 | <0.01 | 0.004 | 0.00 | 0.12 | 0.42 | 0.12 | 270 | 8 | <0.002 | 0.21 | 0.65 | <0.001 | 0.16 | 1.15 |
| | BEl | 39-45 | <0.01 | 0.004 | 0.01 | 0.10 | 0.32 | 0.47 | 383 | 31 | <0.002 | 0.50 | 0.47 | <0.001 | 0.31 | 0.75 |
| | 2Bl | 60-70 | <0.01 | 0.002 | 0.02 | 0.02 | 0.10 | 0.48 | 87 | 13 | <0.002 | 0.75 | 0.25 | <0.001 | 0.10 | 0.85 |
| | 2BClk | 80-90 | <0.01 | 0.004 | 0.01 | 0.02 | 0.15 | 0.40 | 74 | 9 | <0.002 | 0.70 | 0.43 | <0.001 | 0.08 | 0.60 |
| | 2Clk | 110-120 | <0.01 | 0.003 | 0.01 | 0.02 | 0.08 | 0.25 | 25 | 6 | <0.002 | 0.44 | 0.55 | <0.001 | 0.06 | 0.41 |
| | 2Clk | 200 | <0.01 | 0.002 | 0.05 | 0.07 | 0.05 | 0.20 | 26 | 40 | <0.002 | 0.32 | 0.40 | <0.001 | 0.08 | 0.49 |
| Compounds bound with complexes (F2) | | | | | | | | | | | | | | | |
| Summit | OAh | 2-6 | 0.16 | 0.179 | 0.315 | 1.21 | 0.92 | 4.03 | 1511 | 820 | 0.008 | 2.74 | 21.4 | 0.011 | <0.0001 | 30 |
| | E | 20-30 | 0.04 | 0.003 | 0.003 | 0.74 | 0.19 | 0.24 | 342 | 49 | 0.011 | 0.09 | 1.2 | 0.003 | <0.0001 | 0.3 |
| | BE | 45-55 | 0.11 | 0.008 | 0.011 | 3.75 | 0.19 | 0.65 | 772 | 213 | 0.0175 | 0.20 | 1.8 | <0.0005 | <0.0001 | 0.2 |
| | 2Btk | 70-90 | 0.13 | 0.006 | 0.041 | 3.71 | 0.16 | 0.60 | 445 | 301 | 0.0305 | 1.15 | 2.8 | <0.0005 | <0.0001 | 0.7 |
| | 2BCk | 110-130 | 0.14 | 0.008 | 0.123 | 3.38 | 0.20 | 1.06 | 254 | 399 | 0.0315 | 6.02 | 3.0 | <0.0005 | <0.0001 | 1.3 |
| | 2BClk | 150-170 | 0.06 | 0.001 | 0.010 | 3.44 | 0.20 | 0.84 | 86 | 321 | 0.008 | 5.27 | 1.1 | <0.0005 | <0.0001 | 0.6 |
| | 2Clk | 200 | 0.06 | 0.001 | 0.002 | 0.94 | 0.20 | 0.80 | 72 | 36 | <0.001 | 2.22 | 0.9 | <0.0005 | <0.0001 | 0.7 |
| Backslope | OAh | 2,5-4 | 0.22 | 0.142 | 0.420 | 2.03 | 1.28 | 4.01 | 1249 | 2583 | 0.031 | 2.13 | 26.5 | 0.007 | <0.0001 | 43 |
| | Ah | 5-10 | 0.14 | 0.115 | 0.130 | 1.71 | 0.34 | 1.53 | 2286 | 1005 | 0.05 | 1.04 | 20.8 | 0.011 | <0.0001 | 9.9 |
| | AhE | 12-18 | 0.10 | 0.038 | 0.045 | 0.63 | 0.39 | 0.81 | 1549 | 232 | 0.037 | 0.66 | 8.9 | 0.013 | <0.0001 | 4.8 |
| | E | 30-40 | 0.03 | 0.006 | 0.002 | 0.63 | 0.14 | 0.33 | 273 | 48 | 0.0165 | 0.05 | 0.9 | 0.004 | <0.0001 | 0.2 |
| | EB | 52-62 | 0.08 | 0.003 | 0.003 | 1.05 | <0.0011 | 0.35 | 314 | 73 | 0.0175 | 0.02 | 0.8 | <0.0005 | <0.0001 | 0.1 |
| | El | 75-85 | 0.10 | 0.005 | 0.014 | 1.27 | 0.24 | 0.36 | 370 | 124 | 0.0195 | 0.68 | 1.1 | <0.0005 | <0.0001 | 0.2 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Backslope | 2Btl | 104-114 | 0.06 | 0.003 | 0.050 | 3.73 | 0.19 | 0.84 | 239 | 323 | 0.031 | 2.82 | 3.3 | <0.0005 | <0.0001 | 0.3 |
| | 2BCl | 140-150 | 0.12 | 0.008 | 0.107 | 3.83 | 0.19 | 1.14 | 250 | 407 | 0.055 | 4.51 | 6.9 | 0.008 | <0.0001 | 1.5 |
| | 2Cl | 200 | 0.06 | 0.003 | 0.040 | 3.11 | 0.19 | 0.80 | 128 | 291 | 0.0165 | 3.92 | 2.0 | <0.0005 | <0.0001 | 1.1 |
| Footslope | Ah | 9-14 | 1.41 | 0.145 | 0.320 | 0.99 | 1.01 | 4.49 | 10374 | 9.4 | 0.044 | 2.85 | 23.7 | 0.030 | <0.0001 | 7.5 |
| | AhE | 17-20 | 0.08 | 0.014 | <0.0002 | <0.0001 | 0.54 | 0.69 | 244 | 0.3 | 0.0135 | 0.36 | 2.5 | <0.0005 | <0.0001 | 1.4 |
| | E | 25-35 | 0.09 | 0.002 | 0.005 | <0.0001 | 0.79 | 0.22 | 270 | 0.01 | 0.0013 | 0.04 | 1.2 | <0.0005 | <0.0001 | 0.2 |
| | Btg | 48-58 | 0.12 | 0.008 | 0.045 | 3.17 | 0.12 | 1.30 | 426 | 404 | 0.022 | 3.12 | 1.8 | <0.0005 | <0.0001 | 1.0 |
| | BCl | 100 | 0.16 | 0.006 | 0.045 | 2.13 | <0.001 | 0.62 | 146 | 278 | 0.0185 | 1.91 | 2.2 | <0.0005 | <0.0001 | 1.5 |
| Toeslope | Ha | 0-8 | 0.30 | 0.125 | 0.229 | 0.39 | <0.001 | 5.23 | 3490 | 8.0 | <0.001 | 2.12 | 19.1 | <0.0005 | <0.0001 | 10 |
| | HaE | 8-12 | 0.14 | 0.014 | <0.0002 | <0.0001 | 0.34 | 0.69 | 874 | 0.01 | <0.001 | 0.28 | 2.4 | <0.0005 | <0.0001 | 0.1 |
| | E | 17-23 | 0.10 | 0.003 | 0.005 | <0.0001 | 0.66 | 0.23 | 343 | 0.3 | <0.001 | 0.07 | 1.0 | <0.0005 | <0.0001 | 0.5 |
| | E | 28-35 | 0.07 | 0.005 | 0.004 | 0.08 | 0.77 | 0.36 | 383 | 2.6 | 0.0085 | <0.003 | 0.9 | <0.0005 | <0.0001 | 0.7 |
| | BEl | 39-45 | 0.06 | 0.006 | 0.007 | 3.64 | 0.27 | 2.39 | 561 | 232 | 0.01 | 0.27 | 1.7 | <0.0005 | <0.0001 | 0.3 |
| | 2Bl | 60-70 | 0.09 | 0.006 | 0.119 | 3.67 | 0.38 | 1.98 | 469 | 672 | 0.042 | 5.27 | 2.0 | <0.0005 | <0.0001 | 0.8 |
| | 2BClk | 80-90 | 0.08 | 0.005 | 0.048 | 3.42 | 0.22 | 1.01 | 357 | 353 | 0.0245 | 2.47 | 2.5 | <0.0005 | <0.0001 | 0.6 |
| | 2Clk | 110-120 | 0.06 | 0.003 | 0.023 | 2.07 | 0.13 | 0.61 | 149 | 158 | 0.0215 | 1.14 | 1.9 | <0.0005 | <0.0001 | 0.5 |
| | 2Clk | 200 | 0.06 | 0.003 | 0.065 | 4.12 | 0.19 | 0.71 | 110 | 328 | 0.008 | 4.30 | 2.2 | <0.0005 | <0.0001 | 0.9 |
| Compounds bound with Fe and Mn (hydr)oxides (F3) | | | | | | | | | | | | | | | |
| Summit | OAh | 2-6 | 0.26 | <0.0001 | 0.455 | 1.2 | 0.7 | 3.8 | 904 | 893 | <0.002 | 3.0 | 25.8 | 0.019 | 0.048 | 43.0 |
| | E | 20-30 | 0.26 | 0.011 | 0.031 | 2.3 | 2.9 | 0.8 | 5316 | 219 | <0.002 | 0.4 | 5.5 | <0.001 | 0.089 | 3.9 |
| | BE | 45-55 | 0.20 | 0.020 | 0.019 | 1.8 | 2.7 | 2.6 | 3815 | 127 | <0.002 | 1.1 | 4.7 | <0.001 | 0.209 | 5.5 |
| | 2Btk | 70-90 | 0.02 | 0.011 | 0.024 | 0.9 | 2.7 | 2.3 | 2403 | 56 | <0.002 | 1.2 | 3.4 | <0.001 | 0.134 | 8.3 |
| | 2BCk | 110-130 | 0.04 | 0.008 | 0.073 | 1.6 | 3.7 | 2.4 | 1993 | 148 | <0.002 | 5.9 | 2.1 | <0.001 | 0.189 | 11.2 |
| | 2BClk | 150-170 | 0.12 | 0.005 | 0.030 | 1.7 | 1.9 | 1.7 | 1025 | 117 | <0.002 | 4.1 | 1.2 | <0.001 | 0.224 | 6.7 |
| | 2Clk | 200 | 0.05 | 0.006 | 0.015 | 0.8 | 1.2 | 1.6 | 744 | 45 | <0.002 | 2.2 | 2.6 | <0.001 | 0.224 | 5.3 |
| Summit | OAh | 2,5-4 | 0.24 | <0.0001 | 0.390 | 1.5 | 0.0 | 3.9 | 707 | 1787 | <0.002 | 2.1 | 24.0 | <0.001 | 0.020 | 52.0 |
| | Ah | 5-10 | 0.40 | 0.002 | 0.200 | 1.4 | 0.5 | 1.9 | 2259 | 781 | <0.002 | 1.1 | 22.9 | 0.026 | 0.038 | 20.3 |
| | AhE | 12-18 | 0.28 | 0.003 | 0.045 | 0.8 | 1.2 | 1.1 | 2632 | 202 | <0.002 | 0.7 | 10.9 | 0.025 | 0.044 | 4.8 |
| | E | 30-40 | 0.10 | 0.011 | 0.018 | 1.8 | 2.1 | 0.8 | 3897 | 173 | <0.002 | 0.4 | 3.8 | <0.001 | 0.088 | 3.8 |
| | EB | 52-62 | 0.09 | 0.011 | 0.014 | 1.0 | 2.9 | 2.4 | 2972 | 65 | <0.002 | 1.1 | 2.5 | <0.001 | 0.129 | 5.5 |
| | El | 75-85 | 0.09 | 0.013 | 0.020 | 0.7 | 2.8 | 2.3 | 2364 | 51 | <0.002 | 1.3 | 2.3 | <0.001 | 0.114 | 4.6 |
| | 2Btl | 104-114 | <0.002 | 0.004 | 0.028 | 1.1 | 2.9 | 2.2 | 1711 | 64 | <0.002 | 2.4 | 3.7 | <0.001 | 0.099 | 6.8 |
| | 2BCl | 140-150 | <0.002 | 0.007 | 0.044 | 1.7 | 2.8 | 2.2 | 1950 | 120 | <0.002 | 3.6 | 4.3 | <0.001 | 0.124 | 9.9 |
| | 2Cl | 200 | 0.09 | 0.007 | 0.045 | 1.7 | 1.9 | 1.8 | 1421 | 128 | <0.002 | 3.3 | 2.2 | <0.001 | 0.204 | 7.2 |
| Footslope | Ah | 9-14 | 0.37 | <0.0001 | <0.0001 | 0.0 | 0.3 | 2.1 | 2394 | 0 | <0.002 | 0.9 | 7.4 | <0.001 | <0.0001 | 1.4 |
| | AhE | 17-20 | 0.12 | <0.0001 | 0.036 | 0.1 | 1.0 | 1.0 | 325 | 6 | <0.002 | 0.6 | 4.6 | <0.001 | 0.084 | 1.7 |
| | E | 25-35 | 0.10 | 0.001 | 0.004 | 0.1 | 1.4 | 0.3 | 558 | 8 | <0.002 | 0.2 | 1.7 | <0.001 | 0.094 | 1.5 |
| | Btg | 48-58 | 0.16 | 0.009 | 0.038 | 2.3 | 3.5 | 3.7 | 3589 | 197 | <0.002 | 3.8 | 2.6 | <0.001 | 0.114 | 7.1 |
| | BCl | 100 | 0.05 | 0.007 | 0.028 | 1.3 | 3.4 | 2.1 | 1728 | 106 | <0.002 | 2.6 | 1.7 | <0.001 | 0.134 | 8.2 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Toeslope | Ha | 0-8 | 0.13 | <0.0001 | 0.149 | 0.2 | 0.0 | 4.3 | 1257 | 3 | <0.002 | 1.4 | 13.0 | <0.001 | 0.006 | 10.2 |
| | HaE | 8-12 | 0.17 | <0.0001 | 0.025 | 0.1 | 0.8 | 1.1 | 592 | 5 | <0.002 | 0.4 | 4.1 | <0.001 | 0.056 | 2.1 |
| | E | 17-23 | 0.15 | 0.000 | 0.010 | 0.1 | 1.1 | 0.3 | 665 | 9 | <0.002 | 0.1 | 1.6 | <0.001 | 0.074 | 0.9 |
| | E | 28-35 | 0.20 | 0.008 | 0.013 | 0.7 | 1.7 | 0.7 | 2182 | 50 | <0.002 | 0.3 | 2.8 | <0.001 | 0.144 | 2.3 |
| | BEl | 39-45 | 0.07 | 0.011 | 0.017 | 2.6 | 3.6 | 2.4 | 4988 | 184 | <0.002 | 1.2 | 4.5 | <0.001 | 0.204 | 5.1 |
| | 2Bl | 60-70 | 0.14 | 0.009 | 0.047 | 1.0 | 3.0 | 3.1 | 3010 | 97 | <0.002 | 2.7 | 2.5 | <0.001 | 0.139 | 7.1 |
| | 2BClk | 80-90 | 0.07 | 0.008 | 0.022 | 1.1 | 3.6 | 2.7 | 2705 | 75 | <0.002 | 2.3 | 3.2 | <0.001 | 0.109 | 7.4 |
| | 2Clk | 110-120 | <0.002 | 0.004 | 0.015 | 0.8 | 2.4 | 1.9 | 1517 | 37 | <0.002 | 1.6 | 2.3 | <0.001 | 0.054 | 4.9 |
| | 2Clk | 200 | 0.02 | 0.013 | 0.032 | 1.1 | 1.8 | 1.7 | 1229 | 84 | 0.052 | 3.1 | 1.7 | <0.001 | 0.189 | 6.1 |

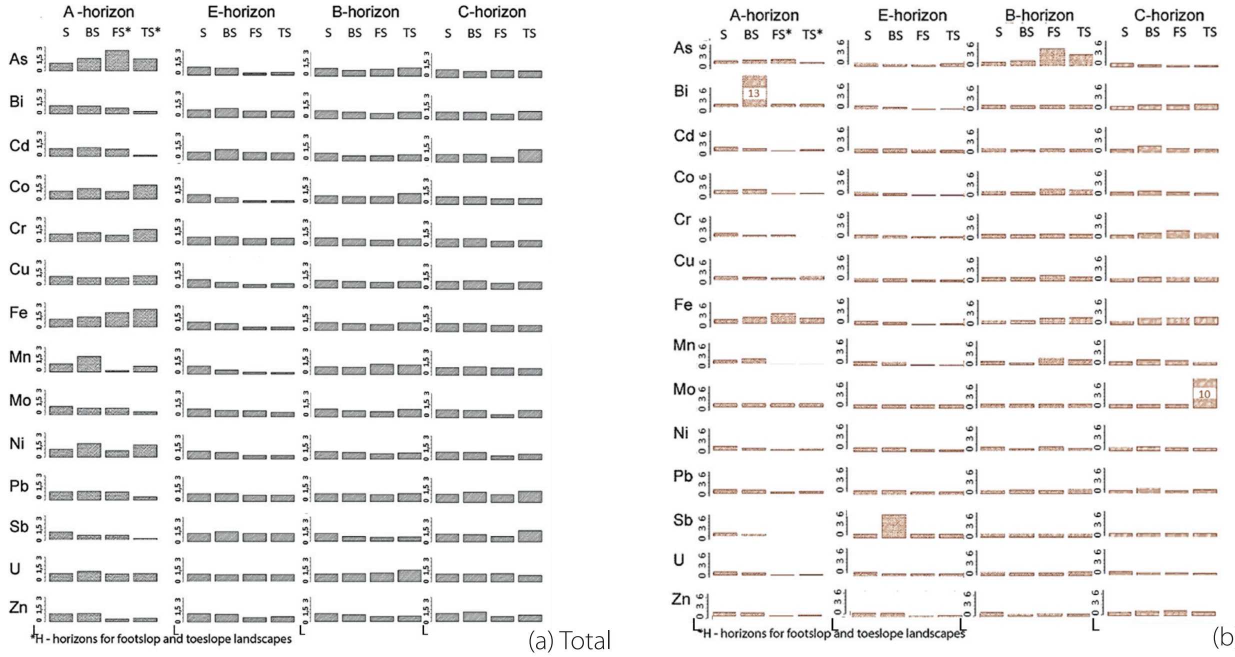


(a) Total



(b) F3

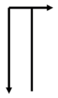
**Fig. B.1. The vertical differentiation (R) of the total content (a) and the F3 fraction (b) of the HMMs of the soils of the catena**



(a) Total (b) F3

**Fig. B.2. The spatial differentiation (L) of total content (a) and the F3 (b) fraction of the HMMs of the soils of the catena**

**Table A.4. Vertical differentiation of the HMMs in the Retisols studied**

| HMMs fractions | Accumulative | Accumulative-eluvial-illuvial | Eluvial | Subsoil-accumulative | Undifferentiated |
|---|---|---|---|---|---|
| |  |  |  |  |  |
| SUMMIT. Endocalcaric Albic Neocambic Stagnic Glossic Retisols | | | | | |
| Total | **Cd Bi*** | **Sb Zn** | **As Co Cu Fe** U | Ni | |
| F1 | **As Cd Mn Mo Pb Zn** | Bi | **Cr Cu Fe** U | Co **Ni** | Sb |
| F2 | **Cr Cu Zn** Fe Mo **Pb** Sb | As Bi Cd Mn | Co | Ni | U |
| F3 | **Pb Sb** | **As Cd** Co **Cu** Mn Ni **Zn** | **Cr Bi** | Fe | Mo U |
| BACKSLOPE. Endocalcaric Albic Neocambic Stagnic Glossic Retisols | | | | | |
| Total | **Cd** | Bi Mn Mo Pb **Sb Zn** | As **Co Cr Cu Fe** Ni | - | U |
| F1 | **As Bi Cd  Mn Zn Cr Pb** | Co **Cu** | **Fe** U | **Ni** | Mo Sb |
| F2 | **Bi Cd Cr Cu** Mn **Zn As Pb** | Mo **Ni** Sb | Co Fe | - | **U** |
| F3 | Cd Mn Zn As **Pb Sb** | **Cu** | **Bi Fe Cr** | - | Co **Mo** Ni U |
| FOOTSLOPE. Endocalcaric Glossic Albic Gleyic Histic Stagnosols | | | | | |
| Total | As **Bi Cd** | Mo Pb **Sb** | **Co Cr** Fe Mn Ni U | - | Cu |
| F1 | **As Pb Cr** Fe **Bi** | Cd **Co** Mn **Ni** Zn | **Cu** | U | **Mo Sb** |
| F2 | **As Cd** Cr Mo **Pb** Sb **Zn Bi** | Cr Cu Fe **Ni** | - | Co **Mn** | U |
| F3 | - | **As Cd Cu** Fe **Pb** | U | Bi Co Cr Mn Ni | **Mo** Sb Zn |
| TOESLOPE. Endocalcaric Glossic Albic Gleyic Histic Stagnosols | | | | | |
| Total | Ni | - | **As Co Cu Cr** Mn U | Pb Sb Bi Cd | Mo Zn |
| F1 | **Cd** Co **Cr** U **Bi Mo Pb Zn** | **Cu Ni** | Cr | - | As Mn **Sb** |
| F2 | **Cd Cr** Ni **Pb Zn** | As Bi Co Cu **Fe** | W | **Mn** Mo | Sb |
| F3 | Ni | **Cd Cu Pb Zn** | As Co **Cr Fe** Mn | - | Bi **Mo** Sb **U** |

Bold - elements, the type of distribution of which is preserved in the soils of two or more positions. Dash - elements with this type of distribution were not found.

**Table A.5. Accumulation of elements at geochemical barriers and correlation with soil properties (in brackets)**

| HMMs fractions | Geochemical barriers | | | Carbonate ($CaCO_3$) | Don't accumulate on barriers |
|---|---|---|---|---|---|
| | Alkaline (pH) | Sorption (clay) | Biogeochemical (SOM) | | |
| Total | $As_{0.32}$ $Co_{0.42}$ $Cr_{0.43}$ $\mathbf{Cu_{0.64}}$ $Fe_{0.55}$ $Mn_{0.23}$ $Ni_{0.68}$ | $As_{0.32}$ $Co_{0.36}$ $Cr_{0.49}$ $\mathbf{Cu_{0.55}}$ $Fe_{0.51}$ $Ni_{0.54}$ $Zn_{0.22}$ | $Pb_{0.38}$ $S\mathbf{b_{0.19}}$ | - | Bi Cd *Mo* U |
| F1 | $\mathbf{Cu_{0.44}}$ $Ni_{0.47}$ | $\mathbf{Cu_{0.33}}$ $Ni_{0.32}$ | $As_{0.32}$ $Bi_{0.59}$ $Cd_{0.39}$ $Co_{0.6}$ $Cr_{0.29}$ $Fe_{0.38}$ $Mn_{0.2}3$ $Pb_{0.63}$ $\mathbf{Sb_{0.26}}$ $Zn_{0.54}$ | $Co_{0.62}$ $Ni_{0.56}$ | U |
| F2 | $Cd_{0.20}$ $Co_{0.50}$ $\mathbf{Cu_{0.41}}$ | $Co_{0.32}$ $\mathbf{Cu_{0.24}}$ | $As_{0.23}$ $Bi_{0.44}$ $Cr_{0.53}$ $Fe_{0.54}$ $\mathbf{Sb_{0.33}}$ $Zn_{0.31}$ | - | Mn *Mo* Ni Pb |
| F3 | $Cr_{0.40}$ $\mathbf{Cu_{0.34}}$ $U_{0.40}$ $Zn_{0.45}$ | $Cr_{0.26}$ $\mathbf{Cu_{0.21}}$ $U_{0.35}$ $Zn_{0.4}$ | $As_{0.30}$ $Mn_{0.20}$ $Pb_{0.20}$ $\mathbf{Sb_{0.37}}$ | - | Bi Cd Co Fe Mo Ni |

Numbers - values r with p value <0.05. Bold (italic) - elements that in all (three of four) forms accumulate at the same geochemical barrier.