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Róbert Pánik

THE ORIGIN OF PODZOLS

AND

DISTRIBUTION OF ELEMENTS INDUCED BY PODZOLIZATION

Vznik podzolů a distribuce prvků ovlivněná podzolizací

Bakalářská práce

Vedoucí bakalářské práce: prof. RNDr. Martin Mihaljevič, Csc.

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Prohlášení:

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V Praze, dne

Podpis

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Summary

Part I. The purpose of this work is to review publications and present a novel approach to the interpretation of available data in attempt to explain process of podzolization. First, we consider all major inputs that affect podzol formation from global to microscopic scale - climate, parent material, vegetation, mycorrhizal fungi, and fire regime in the podzol areas. Important role of fire-produced charcoal in the podzolization process due to its specific properties is also considered. Subsequently, physico-chemical transitions upon the downward progression of podzolization front (i.e., C to Bs, Bs to Bhs, and Bhs to E) are treated, in conjunction with the characterization of secondary phases that precipitate in the Bs horizon, as well as the demonstration of the major role of organic matter in the formation of podzols. Organic carriers exuded by plants and fungi are shown both to decrease mobility of certain elements (e. g., Ca, Al) by the formation of secondary solid phases, and also to increase mobility of otherwise unavailable elements (e.g., Fe) by their chelating abilities. Special emphasis is given to siderophores, group of organic substances that show high and specific affinity for Fe^{3+} chelation over a wide range of pH. Finally, spatial and temporal trends of podzolization and podzol chemistry are treated, revealing relations in the relative proportion of organic and inorganic transport and subsequent immobilization as a result of environmental specifics.

Part II. Vertical distribution of bulk concentrations and exchangeable portions of selected elements and organic matter in intrazonal podzol were studied by ICP-MS, ICP-OES, loss-on-ignition, and micromorphology. Results show high degree of parent material weathering and nutrient depletion, with the values of Ba/Sr (weathering index) in the range of 7.2 to 9.5, showing relative maxima in E horizons and minima in A and Bhs horizons. Despite the absence of reducing conditions in the studied podzol, behaviour of Fe shows high correlation with that of low field strength elements, indicating its transport in a reduced state. Most depleted of studied elements is Mn, which shows highest rates of uptake by plants and subsequent remobilization from the topsoil. Overall order of eluvial-illuvial redistribution of studied elements is Fe > Rb > Sr > Eu > Mn > light lanthanides > Y. Normalization of elemental concentrations in individual horizons to those in horizons from which they developed (i.e., Bs/C, Bhs/Bs, E/Bhs) was employed in order to reveal changes that take place during the downward progress of podzolization front. Lanthanide patterns of illuvial horizons show positive Eu anomalies, while patterns of eluvial horizons show inverse character with substantial negative Eu anomalies. Relative maximum of Fe concentrations was found in Bs horizons, while relative maxima of organic carbon, exchangeable acidity, base saturation, as well as Rb, Sr, and to a lesser degree Ba concentrations were found in Bhs horizons. pH minima in the illuvial horizon seem to be characteristic feature of intrazonal podzols, compared to zonal podzols where pH increases continuously with depth. Micromorphological study showed high degree of feldspar weathering in E horizons, dominance of root-derived organic matter in Bhs horizons, and monomorphic coatings of secondary Fe phases in Bs horizons, indicating their precipitation from the soil solution. Charcoal particles were present in all studied horizons, showing an important role of recurring fire events in the study area.

Abstrakt

Část I. Cílem této práce je recenze publikací a užití nového přístupu k interpretaci dostupných dat za účelem objasnění procesu podzolizace. Jako první jsou posouzeny hlavní faktory ovlivňující vznik podzolů od globálního po mikroskopické měřítko - podnebí, matečná hornina, vegetace, mykorhizní houby a režim požárů v oblastech výskytu podzolů. Vzhledem k jeho specifickým vlastnostem je dále zvážena i důležitá role uhlí produkovaného při požárech. Následně jsou definovány fyzikálně-chemické přechody v průběhu postupu podzolizačního frontu (t.j., přechod horizontu C do Bs, Bs do Bhs a Bhs do E), ve spojení s charakterizací sekundárních fází srážejících se v Bs horizontu, jako i demonstrací významného vlivu organické hmoty při tvorbě podzolů. Organické nosiče uvolňovány rostlianami a houbami způsobují jak snížení mobility některých prvků (např. Ca, Al) prostřednictvím vzniku sekundárních pevných fází, tak zvýšení mobility jinak nedostupných prvků (např. Fe) díky své schopnosti chelace. Zvláštní důraz je kladen na siderofóry, skupinu organických látek vykazujících vysokou a specifickou afinitu pro chelaci Fe^{3+} v širokém rozmezí pH. V poslední části jsou charakterizovány prostorové a časové trendy podzolizace a chemismu podzolů, poukazující na vztahy mezi relativním zastoupením procesů organického a anorganického transportu a náslendé imobilizace jako výsledek specifik daného prostředí.

Část II. Vertikální distribuce celkových a vyměnitelných koncentrací vybraných prvků v intrazonálním podzolu byly analyzovány pomocí ICP-MS, ICP-OES, žíháním a mikromorfologickými metodami. Výsledky poukazují na vysokou míru zvětrání matečné horniny a ochuzení živinami, s hodnotami zvětrávacího indexu Ba/Sr v rozmezí hodnot 7,2 až 9,5, s relativními maximy v E horizontech a minimy v A a Bhs horizontech. Navzdory nepřítomnosti redukčních podmínek v studovaném podzolu, distribuce Fe vykazuje vysokou korelaci s distribucí nekompatibilních prvků, co naznačuje jeho transport v redukovaném stavu. Nejvíc ochuzeným ze studovaných prvků je Mn, který vykazuje nejvyšší míru příjmu rostlinami a následné remobilizace z povrchové vrstvy. Celková míra eluviálně-iluviální redistribuce studovaných prvků je Fe > Rb > Sr > Eu > Mn > lehké lanthanidy > Y. Za účelem charakterizace změn, které nastávají v průběhu postupu podzolizačního frontu byly koncentrace prvků v jednotlivých horizontech normalizovány koncentracemi v podloží, z kterého tyto horizonty vznikly (t.j. Bs/C, Bhs/Bs, E/Bhs). Lanthanidové vzory iluviálních horizontů vykazují pozitivní Eu anomálie, zatímco vzory eluviálních horizontů mají inverzní charakter s podstatnými negativními Eu anomáliemi. Relativní maxima koncentrace Fe byly nalezeny v Bs horizontech a relativní maxima organického uhlíku, výměnné acidity, saturace bázemi, koncentrací Rb, Sr a v menší míře i Ba v Bhs horizontech. Minima pH v iluviálním horizontu se zdají být charakteristickým prvkem intrazonálních podzolů, v porovnání se zonálními podzoly, kde pH plynule roste s hloubkou. Mikromorfologie ukázala vysoký stupeň zvětrání živců v E horiozntech, dominanci organické hmoty odvozené z kořenů v Bhs horizontech a monomorfní povlaky sekundárních fází Fe v Bs horizontech, indikující jejich srážení z půdního roztoku. Částice uhlí byly přítomny ve všech studovaných horizontech, poukazujíc na důležitou roli periodických požárů v studované oblasti.

Contents

Earth is still in her swaddling clothes, and stretches forth baby fingers on every side.

– Henry David Thoreau, Walden (1854)

Part I

The origin of podzols

1 Introduction

Process of podzolization is characterized by the redistribution of various elements and organic matter in soil from the eluvial (E) horizon that is being leached, to the illuvial (B) horizon, where leached elements and organic matter accumulate. Mechanisms that govern this redistribution have been extensively studied and various theories were proposed to account for the observations. While some acknowledge the major role of organic substances in the transport of predominantly Al and Fe from the eluvial to illuvial horizon [1], others, in contrast, propose transport in the form of inorganic sols [2]. Suggested mechanisms of a subsequent immobilization and accumulation of transported phases in the illuvial horizon also vary and include inorganic processes such as equilibria of soil solution with solid phases, as well as biotic processes such as microbial degradation of organic carriers [3]. Multitude of observed and proposed mechanisms points to the fact that podzolization is not a single process, but rather an interplay of various factors that contribute to the overall outcome in different proportions, depending on the specifics of a given environment.

In order to evaluate the formation of podzols, we will first consider all inputs that influence processes of podzolization. Next, transitions of parent material composition that take place upon the downward progression of podzolization front will be treated, and finally, spatial and temporal trends of podzolization will be briefly described.

2 Conditions of podzolization

2.1 Climate and parent material

Podzol development is bound to areas of low production and decomposition rate of organic matter and with sufficient amounts of percolating water that accommodates the vertical redistribution characteristic for podzolization. Major areas of podzol occurrence are therefore in the high latitudes of cold and humid boreal region, but also in the higher elevations of lower latitudes that show conditions similar to those of boreal region. Apart from the boreal (zonal) podzols, there are also areas of podzol development in the lowland conditions of temperate region. In contrast to zonal podzols that may form from variable parent materials such as glacial tills, intrazonal podzols are bound to extremely nutrient-poor and well-drained sandy deposits. In both cases, however, the common feature is high portion of quartz content, coarse texture that allows vertical movement of soil solution with dissolved components, and low acid-neutralizing capacity that allows a shift of soil reaction towards the acidic values. These characteristics of climate and parent material also imply slow rates of decomposition of organic matter and absence of biological homogenization that would otherwise diminish the sharp vertical differentiation of podzolic profiles. Moreover, temporal stability of these factors as well as the stability of vegetation cover are essential for the formation of highly developed podzols.

2.2 Vegetation and mycorrhizal fungi

Vegetation cover and its character play a crucial role in determining the rate and degree of podzolization by supplying the soil solution with organic substances capable of chelation, thus driving the eluvial - illuvial redistribution in a podzolic profile. Decomposition of vegetation litter and exudates of roots induce the decrease of soil pH and its maintenance in the acidic range. These conditions are essential for the dissolution of poorly soluble Fe and Al mineral phases and their subsequent transport to the illuvial horizon.

Coniferous forests of boreal zone are typical regions of podzol occurrence. Vegetation of these forests is dominated by pine (*Pinus sp.*) and spruce (*Picea sp.*), with minor portion of deciduous trees represented mostly by birch (*Betula sp.*). Podzols in lowland conditions of temperate zone are bound to the heathlands, with vegetation dominated by ericaceous plants represented by heath (*Erica sp.*), heather (*Calluna sp.*), and bilberry (*Vaccinium sp.*). Heathland areas and the composition of their vegetation are maintained by a frequent recurrence of fires, as the underground vegetative organs of ericaceous plants are capable of withstanding fire events and readily recolonize new stands cleared by fire [4].

Importance of chelating abilities of organic compounds released upon the decomposition of plant litter and specific compounds released by the roots of these plants, is demonstrated by the observations of decreased rate of podzolization and subsequent depodzolization after the change of vegetation. The transformation of heathland into a spruce forest was found to be accompanied by a higher rate of decomposition of organo-metallic complexes [5]. This is caused by the decrease of pH which leads to a greater protonization of organic matter. As a consequence, higher amounts of Al are released by complexes and lost from the illuvial horizon. Thus, the released fraction no longer contributes to the processes in illuvial horizon and depodzolization is initiated. Due to its often relatively short turnover times, organic matter is the most sensitive indicator of diminishing rates of podzolization and increase of microbial degradation. Upon the colonization of former heathland by birch, a shift towards younger carbon in the B horizon caused by microbial mineralization was already apparent after 40 years of birch growth [6].

As the parent materials from which podzols develop are often extremely low in available nutrients, plants growing on these substrates must - in order to meet their nutritional requirements - employ methods of nutrient acquisition from otherwise unavailable mineral sources. They achieve this by forming symbiotic associations between their roots and fungi. This mutualistic relationship is called mycorrhiza and in a coniferous forests of boreal zone virtually all of the fine roots are colonized by mycorrhizal fungi, often with a wide variety of associated genera [7]. Highest proportion of roots colonized by mycorrhizal fungi is found in the most nutrient-poor substrates [8]. Acquisition of nutrients for utilization by fungus and its host plant is accomplished through the dissolution of otherwise poorly soluble mineral phases. This is done by the exudation of organic compounds by fungal hyphae, some of which have far greater capacity to release cations from a mineral phases than the compounds produced by the roots of their host plant. Fungal exudates include predominantly low molecular weight organic acids, sugars, and peptides [9].

Roots of higher plants are known to release various saccharides, polysaccharides, aliphatic and aromatic organic acids, amino acids, fatty acids, sterols, enzymes, vitamins, growth factors, numerous other substances, anions and cations [10]. Due to this release of myriad of organic substances, plant roots and mycorrhiza with their immediate surroundings form a hot spots of available nutrients utilized by associated bacterial communities [11]. Soil bacteria acquire these nutrients and colonize fungal hyphae, being thus protected against the acidic pH of a bulk soil [12, 13]. They use hyphae as a highways for colonization of favourable soil microsites created and affected by fungal exudation [14, 15]. Particularly in nutrient-poor parent materials with a high portion of quartz, network of fungal hyphae has a significant impact on the numbers of associated soil-dwelling bacteria [16]. However, interactions of fungi with bacteria are not altogether stimulatory. Some hyphal exudates have been shown to induce an inhibition of associated bacterial communities [17].

By the joint action of roots and fungi, various chemical elements are mobilized with markedly different redistribution patterns. Essential nutrients like Mg, K, Ca, and Mn are taken up by plants and are thus recirculated, with the corresponding enrichment in the upper O and A horizons [8]. Opposite trend is observed for the elements inessential or toxic for plants. Redistribution of mobile fractions of Sc, V, Cr, La, and others is therefore dominated by the downward migration and immobilization in the illuvial horizon [18]. Aluminium is a partial exception to this rule, as will be discussed in section 3.2.

Apart from the nutrition provided by the exudative action of roots and mycorrhiza, decomposition of plant residues accumulated in the topsoil also plays an important role in the nutrition of plants, fungi, and associated bacteria. Different types of plant tissues show a marked chemical signatures and upon mineralization serve as a source of different organic compounds. Decomposition of roots is dominantly accompanied by the release of fatty acids and aliphatic biopolymers, leaves are characterized by the release of high contents of lipids, whereas fresh litter is rich in lignin and polysaccharides [19]. These organic substances show widely different levels of resistance to decay and mineralization and therefore differ in their bioavailability for the uptake by plants and fungi. In coniferous forests and heathlands, recurring fires represent an important process by which even a highly resistant organic matter, otherwise marked by slow decomposition, is readily mineralized and mineral nutrition made available for biological consumption.

2.3 Fires and charcoal

Fire and its recurrence in the boreal coniferous forest and heathlands is a driving force of a vegetation succession, structure, and long-term stability, contributing thus largely to the carbon cycle of these ecosystems [20-22]. Importance of fire and charcoal production in podzol areas is apparent from the numerous studies of fire-derived charcoal particles in the podzolic soils in diverse geographical settings [23-28].

Even though the highest portions of charcoal are found in the upper A horizons, its contribution to the gross content of organic matter and its chemistry in this horizons is negligible. In contrast, in podzolic B horizons, charcoal may comprise a considerable portion of the total carbon content and therefore to a great extent influence the chemistry of these horizons [29].

High chemical activity of charcoal in soil is given by its substantial surface area which is a direct consequence of the temperature of its production. With increasing fire temperature, porosity of produced charcoal is generally greater and consequently, surface area is higher [30]. Specific surface area comparable to that of clay minerals (260 - 300 $m^2 g^{-1}$) can be reached in a high-temperature charcoal [31]. As coniferous trees - and pines especially - produce considerable amounts of resin, combustion of their wood is expected to produce higher temperatures and as a result, charcoal of high surface area.

In the nutrient-poor and acidic substrates, where low amounts of clay minerals are available, sorptive and cation exchange properties of charcoal particles may substantially affect quantity and availability of nutrients and organic substances [32, 33].

Upon the addition of charcoal to the soil a shift from acidic towards neutral pH is observed, accompanied by an increase in cation exchange capacity [34,35]. Higher concentrations of released bioavailable nutrients and adsorption of inhibitory substances like phenols on charcoal can therefore reduce nourishment limitations and stimulate growth of fungi and associated microbial communities in nutrient-poor soils [36]. High contents of aromatic structures in charcoal imply its great resistance to microbial degradation and consequent accumulation during recurring fires [32, 37]. Therefore, it represents an important source of a highly stable carbon with mean residence times in the order of thousands of years, with some charcoal samples dating back to the deglaciation [38].

Fire regime is a key factor that determines the amount and distribution of charcoal in podzols. High intensities of fire tend to diminish its contents in the upper layers, whereas frequent recurrence of fire events of lower intensity promotes its accumulation in the deeper portions of mineral soil [39]. Eventual character and pattern of soil carbon pools incorporated in charcoal particles is thus controlled and shaped by the interplay of severity and regime of fire events, vegetation type and its stability, rate of microbial degradation, and the texture of parent material that controls the downward movement of produced charcoal particles.

3 Progression of podzolization front

3.1 Transition from C to Bs horizon

First major step that occurs upon the downward progression of podzolization front is a transformation of initially little-affected matrix of parent material into a framework of minerals with surfaces highly coated and cemented by secondary solid phases of Fe and Al. This transition is accompanied by a marked change of physico-chemical conditions, arising from the specific properties of these newly formed mineral phases.

Negative surface charge of minerals in parent materials, such as those of clays, serve as sorption sites for various positively charged forms of Fe and Al being transported in a soil solution. In podzols, these include mainly free trivalent ions, complexes with organic carriers, and hydrolyzed-polymerized forms. Solubility of a particular form is governed by the pH, degree of saturation, and availability of sorption sites on the soil solid phase constituents. As the first amorphous colloids of Fe and Al start to precipitate, mainly as ferrihydrite and allophane, strong positive feedback is initiated [40, 41]. This positive feedback is based on the poor crystallinity and therefore high specific surface area of these phases, which act as a medium for further precipitation and crystallization of Fe and Al (oxy)hydroxides. Hence, solubility in the podzol Bs horizons will be controlled to a great extent by the equilibration with solid phase, inducing a marked decrease in concentrations of Al, Fe, siderophilic, and other elements in a soil solution leaving the Bs horizon [42-44].

Tendency for the accumulation of Al, Fe, and to a lesser degree Ti, and Mn, in weathering profiles is a direct consequence of their ionic potential. Compared to the readily water-soluble ions with lower ionic potential (e.g., Na^+), and oxocomplex-forming ions of higher ionic potential (e.g., CO_3^{2-}), ions of intermediate charge-to-radius ratio bond strongly to oxygen, but their charge density is insufficient to repel them from each other. As a result, formation of stable (oxy)hydroxides is promoted in oxidative conditions and these elements thus become immobilized.

Allophane, $(Al_2O_3)(SiO_2)_{1.3\text{-}2} \cdot 2.5\text{-}3(H_2O)$, is an amorphous hydrated mineraloid with variable Al/Si ratios and minor amounts of Fe or base cations in its structure. Due to its rapid precipitation, specific surface area is in order of hundreds of $m^2\ g^{-1}$, with lower values found in more Al-rich species [45,46]. Its formation in a highly acid podzol may control the concentration of free Al^{3+} [2]. In certain podzolic soils, however, it is completely absent. Some justification for this observation will be given in the chapter on podzolization trends (section 4). Progressive ordering of allophane leads to the formation of *imogolite*, $Al_2SiO_3(OH)_4$.

Gibbsite, γ-$Al(OH)_3$, is the most common Al-hydroxide in highly weathered soils, where it occurs with *boehmite*, AlOOH. Its formation is governed by gradual crystallization of primary poorly-ordered Al phases. Nevertheless, its lower stability permits a regressive transformation to a less ordered phases [47].

Ferrihydrite, $Fe_2O_3 \cdot 0.5(H_2O)$, is an iron phase that precipitates from a soil solution in the form of nanocrystals, with resulting specific surface areas in podzols ranging up to 800 $m^2\ g^{-1}$ [48]. Consequently, it is unstable and therefore prone to redissolution. This phase may thus have a significant effect on the control of iron pools released into the soil solution.

Goethite, α-FeO(OH), and *hematite*, α-Fe_2O_3, represent the most abundant Fe^{3+} phases found in soils. In humid temperate and boreal regions, however, only goethite is formed in substantial amounts. Crystal sizes of these minerals are in the range of 5 to 100 nm with corresponding high specific surface area ranging from 50 to 300 $m^2\ g^{-1}$ [49]. In contrast to ferrihydrite, goethite and hematite are characterized by much lower solubilities and higher tendency to order with increasing age.

Geochemical behaviour of these phases is closely related and this is further demonstrated by a common observation of partial solid solutions between Al and Fe end-members. Substitutions of Al for Fe in pedogenic goethite may even cause an increase in its stability [50].

Upon the precipitation of highly insoluble phases, a very little dissolution should be observed. This is especially true for the phases of Fe, as pH range of Fe buffer (<3.8) is lower than that of Al buffer (3.8 - 4.2). Despite this precondition, maximum of Fe accumulation in podzols is usually observed to underlay acumulation maximum of Al [19, 42, 51]. When it is considered that many well-drained podzols, not experiencing water-logging, show apparent signs of higher Fe mobility over that of Al, other mechanisms must obviously come into play.

This is where organic matter takes over and crucially affects further progress of podzolization front. Plants, fungi, and bacteria actively induce both rise in solubility of iron (as a response to its deficiency), and decrease in solubility of aluminium (as a response to its toxicity). The former will be treated now, the latter in subsequent section (3.2).

Iron is an essential element engaged in many biochemical reactions in plants. These include formation of chlorophyll, electron transfer during photosynthesis, catalysis, and functioning of various proteins [52]. As already noted, substantial iron pools are present in highly leached soils. However, as they are in insoluble forms, they are inaccessible for uptake by plants. As a response to this iron stress, plants increase its availability either directly by the production of organic chelators stimulating the dissolution of Fe solid phases and mediating its transport to a plant, or indirectly by establishing symbiotic partnerships with mycorrhizal fungi capable of producing siderophores.

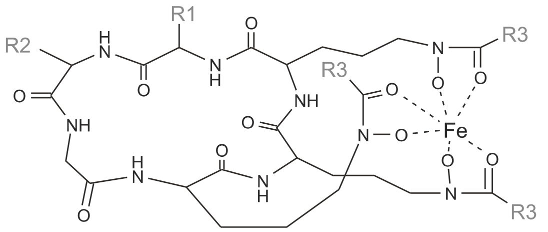
The former mechanism is the most widespread among the plants and is based on the uptake of iron transported in organo-metallic complexes by splitting these complexes with ferric reductase enzymes on the surface of the root cells, release of the organic carrier back to the soil solution, and uptake of the reduced iron by the plant [53-55].

The other mechanism is based on the production of siderophores - organic compounds of various structures with extremely high and specific affinity for chelation of iron over a wide range of pH [56]. Grasses (*Gramineae*) are the only plants capable of siderophore production (therefore called phytosiderophores). All the other plants utilize siderophores produced by their symbiotic fungi and associated microbes [57].

Various siderophores were found to be produced by mycorrhizae of ericaceous plants (typical for heathlands), mycorrhizae of pines (*Pinus*), and were further proved to be present in a soil solutions of podzols [15, 58-62]. These studies clearly show the predominance of hydroxamate siderophores in podzolic environments, especially those of ferrichrome-type (Fig. 1). While bacteria are known to produce diversity of structurally different kinds of siderophores, those produced by fungi are dominated by hydroxamate siderophores [63]. This points to a major role of mycorrhizal fungi in controlling the siderophore pools in podzolic soils. Predominance of ferrichrome-type siderophores in the extreme environment of podzols is a natural consequence of a high environmental stability resulting from their cyclic hexapeptide structure. In the presence of siderophores, their complexation of Fe^{3+} will be favoured over that by organic acids, owing to the higher stability constants of siderophore complex formation [64]. Synergic action with organic acids can, however, greatly enhance the effectivity of iron uptake and transport by siderophores.

In acidic conditions typical for podzols, surfaces of Fe solid phases adsorb free protons from solution. Even though the protonation in the environment of acid soil solution is not sufficient to cause substantial rate of dissolution of these phases, it is the important initial step that promotes the adsorption of organic ligands. Next step is therefore the action of low molecular weight organic acids that, even though showing lower affinity for Fe, help in further destabilization of mineral surfaces. This is done through the interaction of their functional groups (hard Lewis bases) with Fe^{3+} (hard Lewis acid). Upon the release of siderophores, rate of mineral dissolution and its subsequent transport is thus greatly enhanced in comparison with dissolution of unaltered surfaces [65, 66]. In certain plants subjected to iron stress, characteristic diurnal pattern is observed with maximum of siderophore release being preceded by that of organic acids, supporting the notion of the effectivity of their synergic functioning [67].

Many siderophore molecules, however, fail to deliver acquired Fe back to the plant and are lost in a solution, taken up by associated bacteria, or eventually decomposed. Thus, in order to ensure sufficient plant uptake in iron deficient environment, plants produce siderophores in a much higher amounts than they can possibly utilize [68]. This has a substantial impact on the processes in podzolic Bs horizons, as even the smallest amounts of free siderophores produce a disequilibrium, markedly promoting dissolution of Fe solid phases through the ligand complexation and protonation reactions [69]. Release of the iron-free organic ligands upon the Fe uptake of roots in the B horizon, as well as further production of these substances, have a similar effect. This continuous redissolution and transport of Fe, with a subsequent immobilization, saturation, and degradation of organic carrier, will therefore promote gradual movement of zone of precipitated iron phases downwards, with roots following this movement in order to sustain sufficient supply of Fe for plant.



	R1	R2	R3
Ferrichrome	H	H	CH_3
Ferricrocin	H	CH_2OH	CH_3
Ferrichrysin	CH_2OH	CH_2OH	CH_3

Fig. 1. Structure of ferrichrome-type siderophores.

3.2 Transition from Bs to Bhs horizon

Second major step occurring upon the further progression of podzolization front is a change of coating on the surface of mineral grains that is dominated by amorphous Al and Fe solid phases to a coating dominated by organic matter with living roots and root-derived organic biomass in the interstitial spaces.

These forms of organic matter have a different origin, with monomorphic coatings being the product of illuviation, while the polymorphic organic matter between the coated grains is derived mainly from the decay of roots present in this horizon [29]. The reason why the dissolved organic matter transported in a solution from the upper horizons downwards precipitates as coatings, is an abrupt change of physico-chemical conditions on this boundary. Amorphous Al and Fe phases with high specific surface area adsorb dissolved organic matter and thus effectively prevent its further downward transport [70, 71]. Precipitation caused by saturation of organo-metallic complexes was shown to be unlikely due to a low metal-to-carbon ratio found in a soil solution [72]. Presence of roots in this horizon is a natural consequence of their growth in the direction of concentration gradients, following thus the zone of maximum nutrient enrichment. Living biomass of mycorrhizal roots also implies the presence of associated bacteria, causing a gradual decomposition of organic ligands, releasing metals illuviated in organo-metallic complexes [73].

After a passage through the B horizon, composition of dissolved organic matter in a soil solution is significantly changed. While soil solution entering the B horizon contains a wide range of organic compounds of various molecular weight and stability (e.g., lipids, fatty acids, polysaccharides and others), composition of dissolved organic matter in solution leaving this horizon is characterized by lower mean molecular weight of transported compounds and a marked reduction in compounds with aromatic and carboxylic functional groups [19, 70, 74-76]. It is therefore apparent that aromatic and aliphatic structures of higher molecular weight tend to accumulate in the podzol B horizons, and replace a weakly sorbed and less stable ligands that are either redissolved into the soil solution or decomposed by bacteria. Growing proportions of highly resistant organic compounds resulting from this selective adsorption process thus explain higher mean residence times of organic matter in the podzol B horizons [77].

Majority of organic matter in the B horizons of boreal podzols and well-drained podzols in temperate region is represented by a living roots and organic remnants of their decomposition [19, 76, 78]. As those in the surface organic layer, these roots likewise release various exudates in order to increase availability of nutrients for uptake by plant. The most important and abundant of these are anions of dicarboxylic acids: oxalate, citrate, malate, fumarate, and succinate, produced, with an exception of oxalate, as an intermediates of Krebs cycle [79]. Their release is a response to nutrient deficiency, and they increase availability of these nutrients and micronutrients (e. g., base cations, P, Fe, or Mn) by promoting the dissolution of solid phases and blocking the adsorption sites on their surfaces, formation of complexes, or immobilization of cations in the newly formed solid phases [53, 55, 80-83].

Upon the colonization of roots by symbiotic fungi, production of oxalate ($C_2O_4^{2-}$) is substantially increased, and therefore, it is the crucial exudate in mycorrhizal systems of podzols [53, 84, 85]. This is a direct consequence of Al toxicity induced by the plant itself. In order to achieve nutrients availability, pH is reduced by the exudation of organic acids. When cations are eventually transported into the root, however, excess of positive charge causes the exudation of H^+ from the root, driving thus further acidification of soil solution [82, 86]. This in effect increases activity of certain enzymes such as ferric reductase that controls reduction of Fe^{3+} to Fe^{2+}, preferably taken up by plant [87]. As a critical pH value of ~4.2 is reached, however, solubility of Al abruptly rises, and concentration of dissolved Al^{3+} reaches levels that are toxic for plants. Certain mechanisms must therefore exist that ensure alleviation of injurious chemical stress induced by Al^{3+}, while at the same time keep micronutrients like Fe sufficiently available. Plants use two major mechanisms to achieve this state - exclusion and internal Al tolerance.

Exclusion mechanism is based on the exudation of ligands that form stable complexes with Al^{3+} and prevent its transport from soil solution to plant [88, 89]. It is, however, of minor importance in mycorrhizal systems [90].

Internal tolerance mechanism detoxifies Al^{3+} by the transport of organic Al-complexes out of the soil solution and their accumulation in vegetative tissues - predominantly leaves and needles - above the ground [91]. Stable complexes of Al-oxalate - and in some cases Al-citrate - prevent the toxicity of Al^{3+} and can thus be stored in the living plant. This was shown to be the case particularly for the mycorrhizae-utilizing vegetation of podzols, promoting substantial recirculation of Al to the organic layer and its subsequent illuviation to the B horizon [90, 92, 93]. Specific importance of this process for podzolization is further proved by the observation that upon vegetation change that induces depodzolization, Al is no longer immobilized in the B horizon [5]. Continuous input of Al from above is thus one of the reasons for the observed Al accumulation maxima in the B horizon above those of Fe. Nevertheless, this characteristic is not common to all podzolized soils.

Important role of oxalate in the podzolic soils is, however, not limited to its role in the Al tolerance. In nutrient-poor conditions of podzols, oxalate also accommodates immobilization of Ca that would be otherwise quickly lost from the weathering profile. This is accomplished by the formation of Ca-oxalate crystals and their storage on the surface of fungal hyphae and in the various plant tissues [94, 95]. Crystals covering surface of the hyphae represent favourable microsites for growth of bacterial communities, promoting thus the development of mycorrhizae-associated bacteria [95-97]. These, in turn, cause a degradation of organic acids and other exudates in soil solution. Further exudation is therefore enhanced, and this feedback provides bacteria with a constant influx of carbon source [82, 98, 99].

Another source of microenvironments in the mineral matrix of podzols are charcoal particles derived from the forest fires. Contents of these particles in boreal forests can reach values up to 2000 kg ha^{-1} [100]. Highly porous structure of these particles, with many pores of diameters in the order of 10 μm, provides a favourable environment for the fungal hyphae and bacteria [101]. Majority of studies found positive effects of charcoal on the microbial biomass and mycorrhizal colonization in soils [33, 102].

Apart from its function in sustainment of higher pH, CEC, and concentration of available nutrients, positive effect on the plants is achieved also by the sorption of phytotoxins such as phenolics. This process was shown to increase nitrification rates in a forest soils and it is particularly important in areas with ericaceous plants, as these produce high amounts of phenolics [36, 103]. Additionally, bacterial activity leads to decomposition of these phytotoxins, restoring thus capacity of charcoal for their further adsorption [100]. In nutrient-poor acidic conditions of podzols, this function, otherwise furnished by clays, is therefore transferred to a charcoal. Sorptive capacity, however, is highly variable and depends on the production temperature and the age of charcoal particles. Even though the specific surface area is generally higher in high-temperature charcoal, its cation exchange capacity decreases. This is a consequence of gradual loss of O and H from the functional groups and therefore lower charge density on the surface of a particle [31, 104]. Analogous change is expected to take place with increasing age, resulting in only the most recalcitrant aromatic structures being preserved.

3.3 Transition from Bhs to E horizon

The last step in the progression of podzolization front is the removal of organic coatings of minerals, exposing thus their whole surfaces to the dissolving action of organic acids that either percolate from the surface layers or are being actively supplied by the fungal hyphae growing on the mineral grains. Removal of organic coatings may be facilitated by various mechanisms. Apart from the microbial degradation and small rates of redissolution induced by unsaturated organic substances in a soil solution, periodic episodes of water stagnation may play an important role in this process. Especially in the more developed podzols, difference in the pore sizes between leached E horizon and clogged B horizon implies an abrupt decrease in the speed of soil solution percolation. This bottleneck effect produces a narrow zone of water stagnation right above the B horizon, as has been observed for some well-developed podzolic soils [29, 105]. Periodically water-logged uppermost portion of the B horizon is therefore subjected to the most intense downward mobilization, producing often sharp boundary between E and B horizons.

Eluvial horizon, however, is not merely a passive medium for percolation of soil solution. There is a constant influx of organic substances that sustains a considerable pool of predominantly aliphatic organic acids adsorbed on the solid phase of E horizon. These serve as a buffer that readily responds to the fluctuating inputs from the upper layers, maintaining thus the constant metal-to-carbon ratio of the soil solution that enters the B horizon [19, 72, 106]. Part of these organic acids is produced directly in the eluvial horizon by the action of mycorrhizal fungi present in its mineral matrix. Network of the fungal hyphae spreads through this matrix, dominated by quartz, in search of suitable nutrient sources. In a highly weathered profiles, these are represented mainly by feldspars - plagioclase (solid solution of *albite,* $NaAlSi_3O_8$, and *anorthite,* $CaAl_2Si_2O_8$) and potassium feldspar (dominantly *microcline,* $KAlSi_3O_8$). Solubility of these phases is, however, very low. In order to release base cations from the structure of these feldspars, fungi exude dicarboxylic organic acids that greatly increase their solubility [80]. Microcline is the most abundant feldspar in highly weathered profiles, and its structure is characteristic by a cross-hatched twinning, resulting in a three-dimensional network of perpendicular albite lamellae running throughout the bulk of its crystals. Since the albite is more susceptible to weathering, preferential degradation of its lamellae takes place, leading to the formation of characteristic etch pits on the surface of microcline [107, 108]. Fungi use and extend these etch pits, hollowing thus microtunnels (3 - 10 μm wide) that are commonly found in the feldspars of podzol E horizon [109, 110]. Higher amounts of carbon are being allocated to the hyphae growing on the potassium feldspar compared to those on quartz and nutrients acquired from the minerals are transported through mycorrhiza to the host plant [8, 111, 112]. By the dissolution of feldspars, however, large amounts of Al are also being released. Apart from its detoxification in the form of Al-oxalate, this Al was also found to precipitate in the voids of feldspars, together with Si, as illite or kaolinite [96]. Effectivity of mycorrhizal fungi in obtaining nutrients from the solid phases was further demonstrated for hornblende, apatite, and biotite [81, 113, 114]. Thus, extensive extraradical fungal networks enhance the nutrient uptake of their host plants in nutrient-poor environment of podzols by greatly increasing the surface area of mycorrhizal roots and providing access to nutrients like Ca, Mg, K, P, Mn, and Fe, that would be otherwise inaccessible for their uptake.

4 Trends of podzolization

Characteristics of developing podzols, as well as a relative contribution of various podzolization processes, are governed by the environmental specifics of a given area. Moreover, interplay of these factors is variable also in the course of temporal development of podzols. Despite the great diversity, some general trends can be deduced from these observations.

Major geographical trend observed for podzols is a variation of the character of parent material. Zonal podzols in the cold boreal regions with high amounts of precipitation may be formed on various quartz-rich parent materials, often containing portion of less resistant minerals. In contrast, intrazonal podzols of the temperate regions are bound to the nutrient-poor sandy deposits with very little weatherable minerals, dominated by Na,K-feldspars. Geographical distribution of allophane occurrence is a direct consequence of this difference. While it is often found in the podzols of boreal region, allophane is virtually absent in the intrazonal podzols. In order for its precipitation to initiate, soil solution must be supersaturated with respect to allophane. This supersaturation, however, will be attained only by the congruent weathering of minerals with low Si/O ratio such as pyroxenes, amphiboles, or Ca-feldspars [115]. Decreasing trend in concentrations of allophane - and consequently imogolite - is therefore observed from northern to southern podzols [5, 19, 76, 116].

Organic matter as a key factor of podzolization is subjected to a great change of its composition in the course of podzol development. Composition of dissolved organic matter in soil solution changes as it is transported downwards. Less aromatic, hydrophilic substances of lower molecular weight are sorbed weaker than aromatic structures of higher molecular weight [70, 71, 74]. The former, therefore, tend to remain in a soil solution, while the latter are preferentially sorbed to the solid phase. Lower contents of low molecular weight substances in sorbed fraction are further given by their higher availability for microbial degradation. High sorptive capacity of the B horizon thus progressively shifts composition of accumulated organic matter towards the dominance of aromatic structures of higher molecular weight, propagating the formation of fulvic and humic acids [75, 76]. Dissolved organic matter in the soil solution is therefore dominated by aliphatic organic substances of low molecular weight with greatly reduced content of functional groups [70]. Chemistry of organic matter in the E horizon also shifts towards a dominance of aliphatics, most important of these being carboxylic organic acids exuded by mycorrhizal fungi [19]. Composition of its organic content is, however, influenced to a great extent by the input from surface layers that vary with the character of vegetation and decomposition products of its litter. As a consequence of described redistribution of organic substances in the podzol profiles, turnover times of organic matter in the individual horizons differ considerably, with the highest values - in the order of thousands of years - being found in the Bhs horizons [77].

Rate of podzolization, that is, the downward progression of podzolization front, also changes with time. Permeability of the B horizon is being progressively lowered by the illuviated material causing the pore-clogging that limits the degree of remobilization of organic matter, decreasing thus the speed of its further transport downwards [117, 118]. There is, however, no general rule for this mechanism as a disturbances such as fires and vegetation changes may induce episodes of inhibition or even regression of podzolization, producing fluctuations of chemical conditions and contents of organic matter [39, 119].

5 Conclusions

Data reviewed in this work clearly point to the crucial role of biological factors in the development of podzols by influencing the soil pH, rate of mineral weathering, and by the production of organic substances that may both increase and decrease mobility of an individual elements and induce their higher mobilization both upwards and downwards in the podzolic profile. This complex interplay of various biotic and abiotic feedbacks shows that the podzols are not just a simple chromatographic systems and that multidisciplinary study is necessary in order to fully comprehend processes of their formation.

Importance of organic matter in the processes of podzolization further implies a great sensitivity of this soils to the vegetation and land use changes. Podzols that developed in the order of thousands of years throughout the Holocene may thus be relatively rapidly diminished by a higher rate of microbial degradation upon the deforestation or vegetation change. This threat deserves a particular consideration as podzols sequester large amounts of carbon in the form of highly resistant organic substances as well as a considerable pools of charcoal particles.

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Part II

Distribution of elements induced by podzolization

1 Introduction

Processes of podzolization that govern the continuous leaching of eluvial and subsequent enrichment of illuvial horizon affect the distribution of a wide range of elements in a soil profile. Behaviour of individual elements in the course of this redistribution may vary substantially, depending on the chemical properties of a given element and its susceptibility to the various means of transport in the soil solution. As a result, vertical distribution shows characteristics that are specific for the individual element and may be utilized for the interpretation of its geochemical behaviour as well as associated processes of soil formation.

Lanthanide patterns are one of the means widely used for this purpose. While traditionally applied predominantly in the studies of rocks and water, recent works demonstrated their ability to trace many of the processes of pedogenesis [1 - 3]. Fractionation of the lanthanides that takes place upon their release from primary minerals, transport in the soil solution, and subsequent immobilization may thus evidence for such processes as clay leaching, plant cycling, rates of weathering, or occurrence of redox conditions.

Purpose of this work is to investigate a vertical distribution of bulk and exchangeable concentrations of various elements in the profiles of intrazonal lowland podzol and compare the results with other reported data in order to evaluate specifics of processes in the intrazonal podzols, compared to those in the podzols of boreal region. Lanthanide patterns will be further employed in the interpretation of a changes that take place during the progression of podzolization front, and finally, micromorphological study of the individual horizons will be performed in order to determine whether observations correspond to proposed mechanisms of podzolization.

2 Materials and methods

2.1 Study area

The sampling site is situated in the area of Bohemian Cretaceous Basin in the northern Czech Republic (Fig. 1). Morphologically, area represents the sandstone pseudokarst, characterized by the flat planes of altitudes around 300 m a.s.l. with occasional peaty basins and volcanic hills. Sandy and peaty nutrient-poor soils prevailing in the area are dominated by cambisols (arenic, dystric), podzols (arenic, endogleyic), gleysols and psudogleysols (arenic, modal). Vegetation of the study site is a part of a continuous forested enclave (approximately 300 km^2), with the dominance of pine (*Pinus sylvestris*), spruce (*Picea abies*), and birch (*Betula pendula*) [4]. Understory vegetation is represented by the shrubs of *Calluna vulgaris*, *Cytisus scoparius*, and *Vaccinium myrtillus*. Vegetation formation belongs to the biotope of subcontinental pine-oak forests with phytocenosis of the association *Vaccinio vitis-idaeae-Quercetum*, resembling light taigas of Scandinavia. Climate is humid with predominance of the continental features. Mean annual precipitation in the area is 600-700 mm and mean annual temperature ranges from 7 to 8 °C [5]. Local microclimatic conditions cause frequent occurrence of low tempratures and overall character of microsites therefore resembles that of areas in higher altitudes.

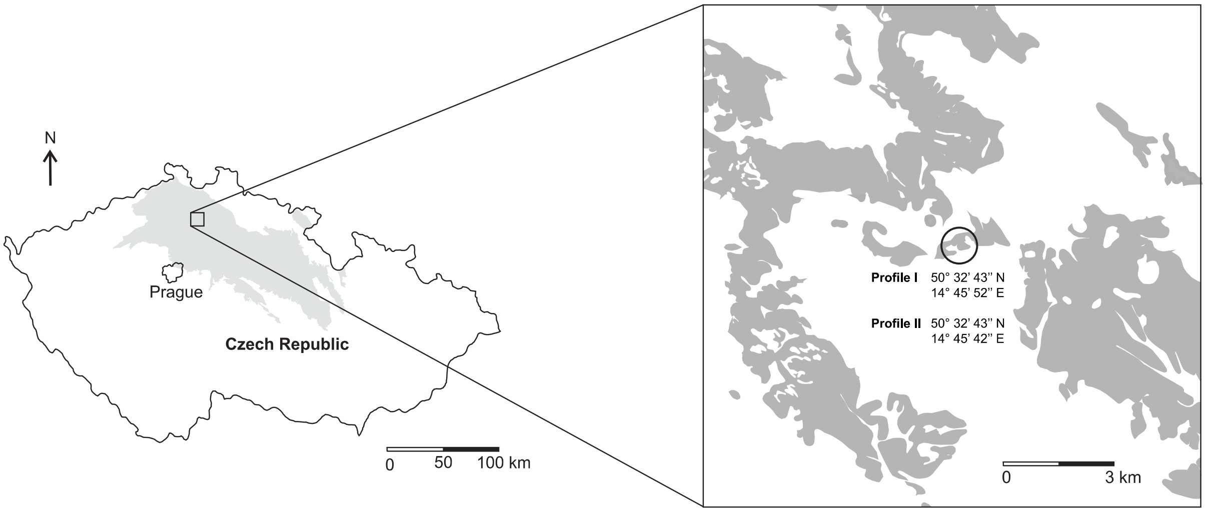


Fig. 1. Left - location of the study area with respect to the Bohemian Cretaceous Basin serving as a source of the parent material for the soil; right - the distribution of arenic podzols in the vicinity of selected sampling site.

2.2 Sampling

Two profiles of (orsteinic) arenic podzol - 200 m apart - were sampled to a depth of 1.5 m. Additional samples of the parent material for both profiles were obtained from a depth of 2.5 m with manual soil auger. Bulk soil material (0.5 kg per sample) was stored in PE bags. Small samples of structurally intact soil were also obtained for the preparation of micromorphological thin sections. All the bulk samples were transported to the laboratory where they were air-dried, homogenised and further treated depending on the method of employed analysis.

2.3 Determination of bulk concentrations

Total concentrations of elements in a bulk soil were determined by the ICP-MS analysis from solutions obtained by acid digestion. 0.2 g of sample pulverised in agate mortar was placed in a Pt crucible with 0.5 ml of $HClO_4$ (70% v/v) and 10 ml HF (50% v/v). Crucible was heated to 170 °C until the evaporation of the acids. Process was repeated with 0.5 ml of $HClO_4$ (70% v/v) and 5 ml HF (50% v/v), and resulting residue was dissolved in HNO_3 (2% v/v), diluted to 100 ml, and stored in PE bottle. Prior to analysis, solution was further diluted with HNO_3 (2% v/v) in proportion 1:9. All chemicals used were of analytical grade. In order to suppress matrix effect and evaluate overall recovery of signal during analysis, two procedural blanks and external standard (SRM 2709a San Joaquin Soil) were prepared by the same procedure along with the samples. For the calibration, 50 ppb multielemental reference standard solution and 20 ppb REE reference standard solution were used. Analytical protocol consisted of two blanks (2% v/v HNO_3), calibration, blank, two procedural blanks, samples, external standard, and quality control with the solutions used for calibration. Correction of count rates was further carried out by the interpolation of ^{74}Ge and ^{103}Rh correction factors. Analysis was performed under the standard analytical conditions (Tab. 1) and analyzed isotopes were chosen with respect to their abundance and extent of isobaric and polyatomic interferences. Overall recovery of external standard certified values obtained by the analysis was 93.4 %.

2.4 Determination of exchangeable cations

Cation exchange capacity was determined by the modified procedure described in [6]. 2.5 g of air-dried soil with the particle size below 2 mm (unsieved bulk samples) was mixed with 30 ml of 0.1 M $BaCl_2$, shaken in PE bottle for 1 hour, subsequently centrifuged at 3000 rpm for 10 minutes and obtained extract was collected to a separate bottle. Procedure was repeated two more times and extract of all three centrifugations was collected to the same bottle. Final extract was diluted to 100 ml with 0.1 M $BaCl_2$. Procedural blank was prepared by the same procedure. Concentrations of exchangeable cations were determined by ICP-OES under the standard analytical conditions (Tab. 1). Additionally, free H^+ was determined in the remaining portion of the extract. 2.5 g of 1 M NaF was added to 50 ml of the extract and the solution was titrated by 0.05 M NaOH to a pH value of 7.8. Amount of free H^+ was then calculated from the equation reported in [6].

2.5 Determination of organic carbon

Content of organic carbon was determined by the loss-on-ignition method described in [7]. 1.2 g of sample was placed in a Pt crucible and oven-dried to a constant weight for 24 hours at 105 °C. Sample was allowed to cool to room temperature in desiccator and dry weight was measured. Sample was then heated to 550 °C for 4 hours, again cooled in a desiccator and weight loss - corresponding to organic carbon - measured.

Table 1
ICP-MS and ICP-OES operating parameters.

	ICP-MS	ICP-OES
Instrument	Thermo Scientific XSeries II	Thermo Scientific iCAP 6500
RF power	1350 W	1150 W
Plasma flow	13.8 l min^{-1} (Ar)	12 l min^{-1} (Ar)
Auxiliary gas flow	0.71 l min^{-1} (Ar)	0.5 l min^{-1} (Ar)
Nebulizer gas flow	0.88 l min^{-1} (Ar)	0.7 l min^{-1} (Ar)
Measured isotopes and spectral lines	^{55}Mn, ^{57}Fe, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd	Al - 167.0 nm, Ca - 315.8 nm, Fe - 238.2 nm, K - 766.4 nm, Mg - 279.5 nm, Mn - 257.6 nm, Na - 589.5 nm

3 Results and discussion

3.1 Concentrations of selected elements

Total concentrations of studied elements determined by ICP-MS with corresponding standard deviations and detection limits are given in Tab. 2 and Fig. 3. These values indicate a high degree of depletion of both soil profiles. Compared to the average concentrations reported for the world soils [8], means of all elements for both profiles show lower values. Depletion is most marked for Mn (43.8x lower concentration than world soil average), Fe (28.6x), Sr (21.4x), Y (14.8x), and Eu (11.7x), with values for other elements being in the depletion range of 4.4-6.4. Most of the values, however, lie in the ranges reported for arenosols [8], with only La concentrations being higher than reported range and concentration of Rb, Y, Eu, and Ba being lower than the arenosol minima. It is therefore apparent that in the course of weathering and pedogenesis, mobility of various elements is different, leading to their relative fractionation in a weathering profile. One of the means to determine the degree of hydrolysis and leaching is a ratio of Ba/Sr. Even though the geochemical behaviour of these alkaline earth metals is very similar, solubility of Sr is higher than that of Ba and therefore, ratio of their respective concentrations tends to grow with increasing degree of weathering [9]. Thus, for the upper continental crust the ratio is 1.95 [10], whereas for the world soil average it rises to 2.63 [8]. Our data show Ba/Sr ratios in the range of 7.2 - 9.5 (Fig. 2), with the relative maxima in the E horizons and minima in A and Bhs horizons indicating higher rate of Sr uptake by plants (due to its similarity to Ca), and its preferential illuviaton from E to Bhs horizon. Similar values for podzol developed on quartzite and gneiss moraine were reported from the southern Sweden [11], even though the values for podzols are usually much lower [12, 13]. These results demonstrate that the development of intrazonal podzols in the temperate region is bound to extremely nutrient-poor substrates.

Compared to the concentrations in parent material from a depth of 2.5 m, average bulk concentrations of Mn, Y, and lanthanides show depletion, while Fe, Rb, Sr, and Ba show enrichment. High values of Spearman's rank correlation coefficient between the members of the latter group, ranging from 0.82 for Sr and Fe to 0.96 for Sr and Ba, indicate that the redistribution of Fe is controlled by similar mechanisms than that of low field strength elements. In order for iron to behave like low field strength element, however, its ionic potential (charge to radius ratio) must be lower than 3, and this is only achieved by the reduction to Fe^{2+}. As reducing conditions are unlikely to occur in a well-drained matrix of studied profiles, reduction of Fe must be accounted for by the different mechanisms.

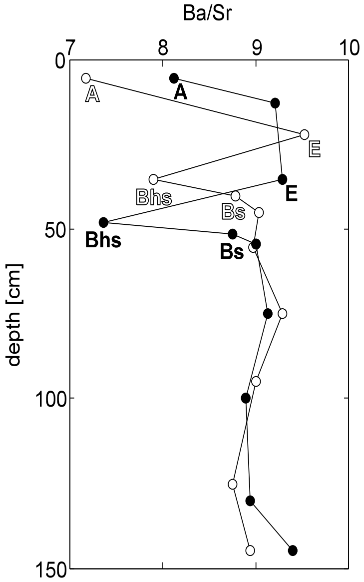


Fig. 2. Ba/Sr concentration ratios in the studied profile I (white) and II (black).

Table 2
Total concentrations of selected elements determined by ICP-MS. Given values represent mean ± standard deviaton.

	Mn	**Fe**	**Rb**	**Sr**	**Y**	**Ba**
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Profile I						
O	61.15 ± 1.46	2078 ± 50	12.40 ± 0.19	15.23 ± 0.24	1.36 ± 0.02	81.6 ± 2.1
A	11.48 ± 0.14	1087 ± 5	7.95 ± 0.06	9.15 ± 0.16	1.72 ± 0.14	65.6 ± 0.9
E	6.55 ± 0.20	198 ± 15	7.51 ± 0.09	5.96 ± 0.07	1.40 ± 0.02	56.8 ± 0.2
Bhs	10.41 ± 0.19	1817 ± 4	22.46 ± 0.15	13.00 ± 0.21	1.71 ± 0.05	102.7 ± 0.7
Bs	8.77 ± 0.18	1881 ± 18	16.98 ± 0.26	10.16 ± 0.03	1.80 ± 0.04	89.2 ± 0.5
Bs/C	10.75 ± 0.10	1821 ± 6	19.28 ± 0.02	10.78 ± 0.13	1.64 ± 0.02	97.4 ± 0.6
C1	12.23 ± 0.33	2004 ± 24	21.25 ± 0.32	12.05 ± 0.19	1.82 ± 0.01	108.2 ± 0.7
C2	13.54 ± 0.29	1610 ± 8	18.70 ± 0.15	10.79 ± 0.08	1.89 ± 0.02	100.4 ± 0.9
Fe band	21.27 ± 0.38	4570 ± 9	19.47 ± 0.05	8.54 ± 0.08	1.72 ± 0.05	63.9 ± 1.0
C3	15.43 ± 0.23	1955 ± 20	13.34 ± 0.06	7.28 ± 0.06	1.93 ± 0.02	65.6 ± 0.4
C4	12.13 ± 0.17	1105 ± 14	14.18 ± 0.20	8.91 ± 0.10	1.41 ± 0.09	78.0 ± 0.6
C5	16.12 ± 0.05	1032 ± 4	10.13 ± 0.14	6.39 ± 0.06	1.19 ± 0.02	57.1 ± 0.6
C6	20.75 ± 0.17	1169 ± 5	10.47 ± 0.16	6.75 ± 0.07	1.86 ± 0.03	59.4 ± 0.3
Profile II						
A	7.55 ± 0.16	341 ± 6	4.64 ± 0.09	5.22 ± 0.05	1.65 ± 0.02	42.4 ± 0.4
A/E	6.15 ± 0.01	177 ± 3	3.75 ± 0.02	3.82 ± 0.04	1.16 ± 0.02	35.2 ± 0.4
E	4.83 ± 0.09	152 ± 2	4.40 ± 0.11	3.93 ± 0.03	1.07 ± 0.01	36.5 ± 0.5
Bhs	8.43 ± 0.18	1321 ± 13	22.47 ± 0.12	11.19 ± 0.09	1.39 ± 0.02	82.2 ± 0.7
Bs	10.08 ± 0.19	2497 ± 40	16.48 ± 0.20	9.45 ± 0.16	1.36 ± 0.01	82.7 ± 0.9
Bs/C	11.59 ± 0.11	1570 ± 11	15.50 ± 0.09	8.69 ± 0.02	1.50 ± 0.03	78.3 ± 0.2
C1	7.59 ± 0.11	1194 ± 11	13.28 ± 0.12	7.48 ± 0.03	1.06 ± 0.02	68.3 ± 0.2
C2	10.43 ± 0.09	906 ± 10	11.24 ± 0.15	6.73 ± 0.09	1.74 ± 0.03	59.8 ± 0.8
C3	10.59 ± 0.11	1059 ± 13	14.46 ± 0.09	8.46 ± 0.07	1.42 ± 0.01	75.7 ± 0.8
C4	15.05 ± 0.22	1046 ± 8	12.80 ± 0.14	7.44 ± 0.18	1.64 ± 0.02	69.9 ± 1.2
C5	14.96 ± 0.20	997 ± 13	11.13 ± 0.04	6.65 ± 0.18	1.71 ± 0.03	62.4 ± 1.1
DL*	0.027	1.1	0.006	0.018	0.003	0.09

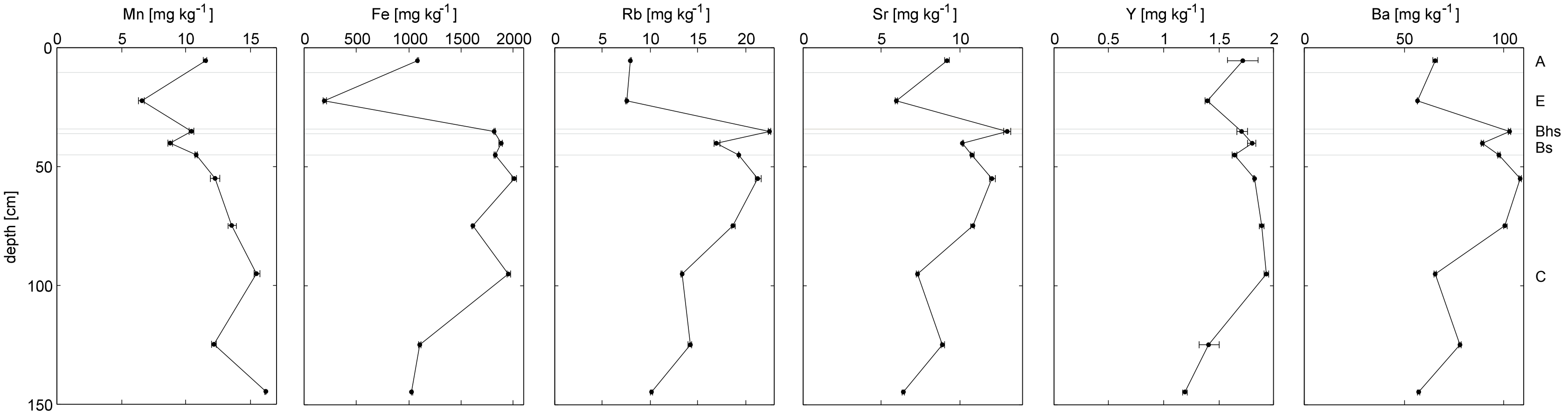
* detection limits calculated as an average 3s levels of two procedural blanks

Table 2
(continued)

	La	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Profile I							
O	5.10 ± 0.13	10.10 ± 0.23	1.18 ± 0.03	4.70 ± 0.15	0.88 ± 0.05	0.10 ± 0.01	0.79 ± 0.04
A	6.32 ± 0.05	12.46 ± 0.10	1.42 ± 0.02	5.71 ± 0.07	1.02 ± 0.03	0.13 ± 0.01	0.91 ± 0.04
E	6.00 ± 0.04	11.77 ± 0.05	1.37 ± 0.02	5.43 ± 0.14	0.96 ± 0.03	0.09 ± 0.01	0.84 ± 0.02
Bhs	6.77 ± 0.05	13.21 ± 0.07	1.48 ± 0.01	5.77 ± 0.15	1.03 ± 0.01	0.14 ± 0.01	0.93 ± 0.04
Bs	7.21 ± 0.08	14.53 ± 0.17	1.67 ± 0.02	6.72 ± 0.09	1.28 ± 0.01	0.16 ± 0.01	1.05 ± 0.03
Bs/C	7.07 ± 0.04	13.96 ± 0.08	1.58 ± 0.02	6.37 ± 0.09	1.19 ± 0.04	0.16 ± 0.01	1.04 ± 0.01
C1	7.39 ± 0.07	14.74 ± 0.12	1.68 ± 0.01	6.71 ± 0.13	1.20 ± 0.03	0.15 ± 0.01	1.07 ± 0.02
C2	8.01 ± 0.06	15.63 ± 0.13	1.77 ± 0.01	6.95 ± 0.13	1.26 ± 0.03	0.16 ± 0.02	1.09 ± 0.04
Fe band	6.37 ± 0.08	11.89 ± 0.04	1.33 ± 0.01	5.15 ± 0.09	0.90 ± 0.01	0.13 ± 0.01	0.84 ± 0.01
C3	8.19 ± 0.11	16.13 ± 0.11	1.84 ± 0.03	7.49 ± 0.57	1.29 ± 0.07	0.14 ± 0.01	1.18 ± 0.04
C4	4.86 ± 0.08	9.57 ± 0.11	1.11 ± 0.03	4.35 ± 0.09	0.83 ± 0.07	0.11 ± 0.01	0.71 ± 0.04
C5	3.95 ± 0.03	8.07 ± 0.08	0.90 ± 0.02	3.62 ± 0.06	0.67 ± 0.02	0.09 ± 0.01	0.57 ± 0.03
C6	6.84 ± 0.07	13.84 ± 0.17	1.53 ± 0.01	6.1 ± 0.03	1.14 ± 0.01	0.13 ± 0.01	0.98 ± 0.02
Profile II							
A	7.15 ± 0.09	14.03 ± 0.10	1.63 ± 0.02	6.40 ± 0.09	1.21 ± 0.04	0.12 ± 0.01	1.06 ± 0.02
A/E	5.03 ± 0.07	10.19 ± 0.12	1.18 ± 0.02	4.77 ± 0.06	0.85 ± 0.04	0.06 ± 0.01	0.75 ± 0.01
E	3.66 ± 0.04	7.34 ± 0.08	0.84 ± 0.01	3.42 ± 0.08	0.66 ± 0.01	0.06 ± 0.01	0.59 ± 0.02
Bhs	5.88 ± 0.03	10.97 ± 0.08	1.23 ± 0.02	4.86 ± 0.09	0.89 ± 0.01	0.13 ± 0.01	0.76 ± 0.04
Bs	6.11 ± 0.10	12.02 ± 0.21	1.36 ± 0.01	5.49 ± 0.08	1.04 ± 0.04	0.13 ± 0.02	0.86 ± 0.02
Bs/C	4.72 ± 0.05	9.39 ± 0.09	1.07 ± 0.01	4.18 ± 0.07	0.79 ± 0.05	0.12 ± 0.01	0.68 ± 0.02
C1	3.79 ± 0.01	7.64 ± 0.05	0.86 ± 0.03	3.45 ± 0.10	0.64 ± 0.04	0.10 ± 0.01	0.55 ± 0.02
C2	7.13 ± 0.04	14.41 ± 0.08	1.64 ± 0.01	6.61 ± 0.11	1.18 ± 0.03	0.11 ± 0.01	1.03 ± 0.03
C3	5.86 ± 0.03	12.00 ± 0.11	1.35 ± 0.03	5.43 ± 0.05	1.00 ± 0.06	0.12 ± 0.01	0.88 ± 0.04
C4	6.83 ± 0.04	13.95 ± 0.06	1.55 ± 0.02	6.15 ± 0.11	1.11 ± 0.05	0.13 ± 0.01	0.95 ± 0.02
C5	7.24 ± 0.06	14.91 ± 0.12	1.61 ± 0.03	6.36 ± 0.12	1.15 ± 0.01	0.12 ± 0.01	0.99 ± 0.04
DL*	0.003	0.005	0.001	0.003	0.003	0.001	0.001

* detection limits calculated as an average 3s levels of two procedural blanks

Profile I



Profile II

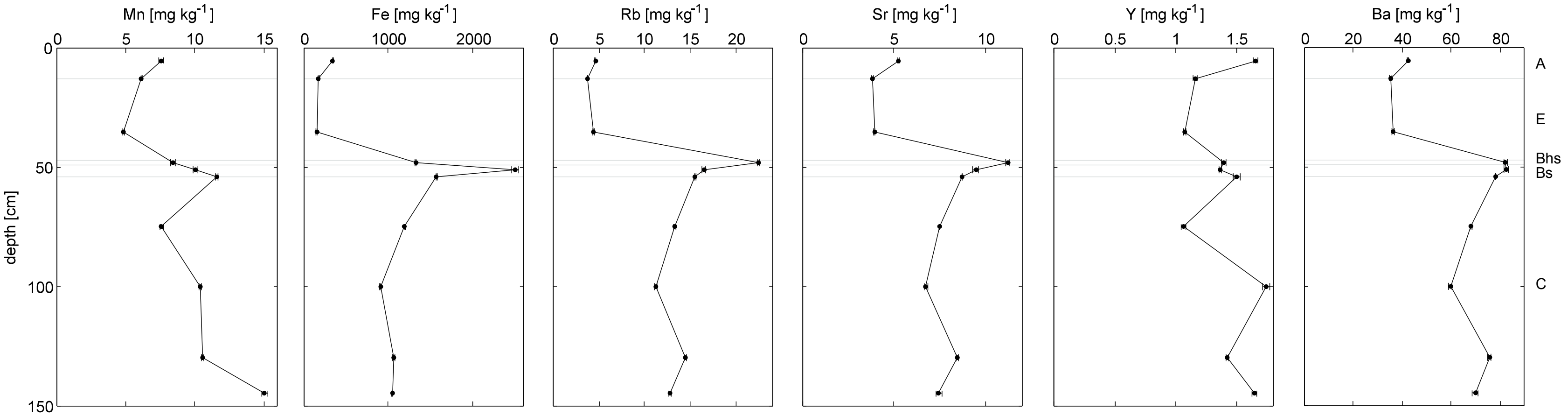
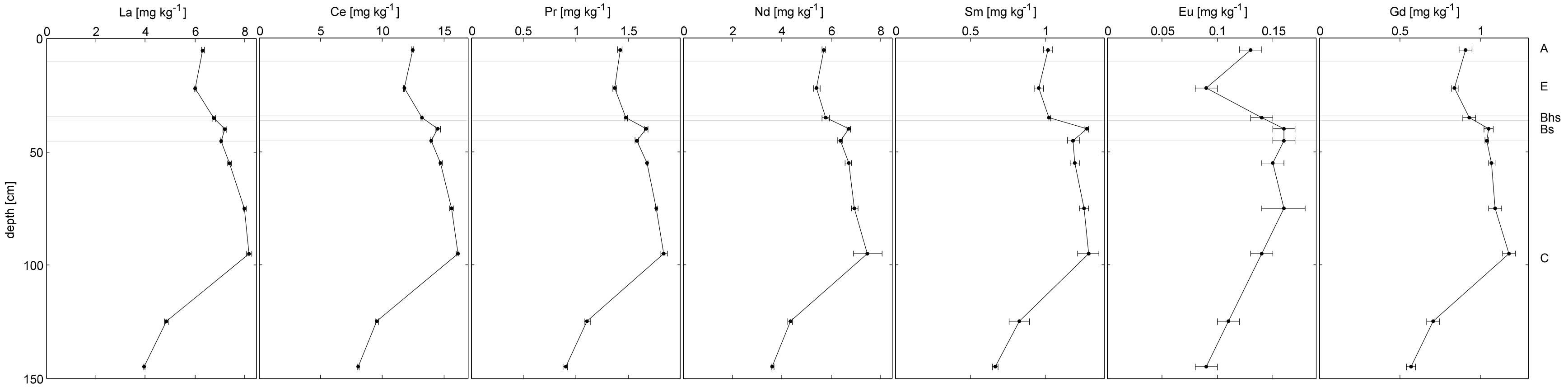


Fig. 3. Total concentrations of studied elements in the bulk soil samples. Error bars represent standard deviation of three ICP-MS measurements.

Profile I



Profile II

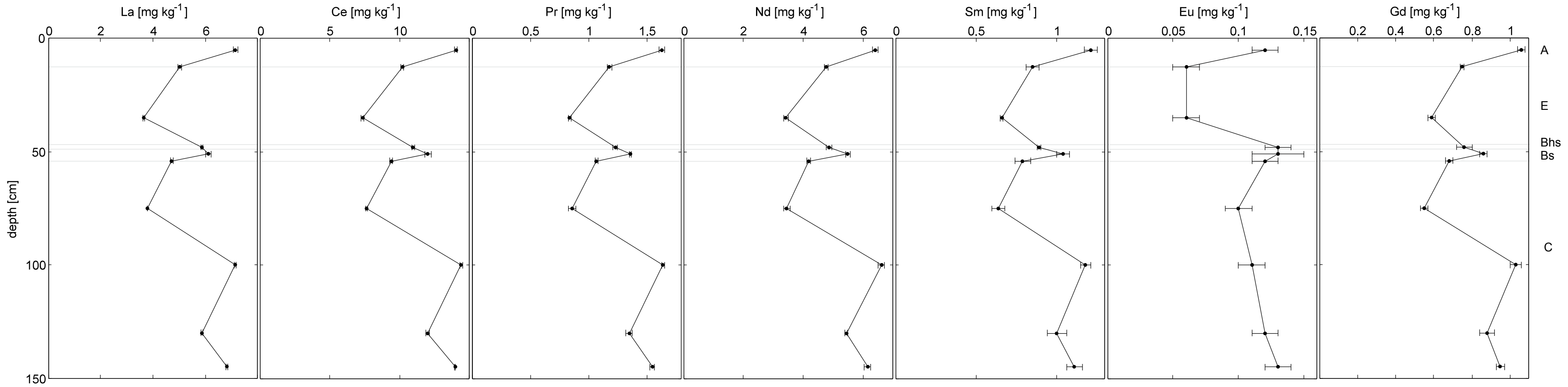


Fig. 3. (Continued)

In nutrient-poor conditions where pools of available Fe are scarce, plants respond to the iron stress by increasing the rate of Fe reduction and uptake through the ferric reductase enzyme in the walls of their root cells [14]. Stimulation of ferric reductase activity is accomplished through the increased influx of protons to the rhizosphere that are being exuded by proton ATPases [15]. Dominance of protons (in ion equivalents) above that of Al^{3+} in the topsoil, rapidly decreasing with depth in both studied profiles (Fig. 4) may be an indication that this process takes place in the studied soil. In order to provide a sufficient amounts of soluble iron for reductase, however, plant responses are not limited to an enhancement of its solubility solely by reducing pH. Low molecular weight organic substances are further being exuded that chelate Fe^{3+} and provide its sufficient supply to the ferric reductase.

Yet another mechanism that may account for increased portions of reduced Fe is decomposition of cellulose by mycorrhizal fungi. This process is also accompanied by the reduction of pH (by the exudation of organic acids), and is based on the production of free radicals that mediate cellulose decomposition [16]. Fungi produce these free radicals through the Fenton reaction by the exudation of glycopeptides containing Fe^{2+} that generate hydrogen peroxide and subsequently free radicals:

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + OH^\bullet$$

By examining the concentrations of studied elements in the litter of profile I and normalizing them to the parent material, it is apparent that biological uptake of Fe, Rb, Sr, and Ba takes place at higher rates than that of Y and lanthanides. Highest rates of plant uptake, however, are observed for manganese. This is explained by the fact that Mn plays an important role in many plant processes. Due to its ability to readily change oxidation state from 2+ to 3+ and 4+, it is utilized in plant redox processes, photosynthesis, and also as a key constituent in the functioning of certain enzymes [15]. Low pH values (<5.5) also favour Mn availability for plant uptake (Tab. 3). Its higher contents in the litter are, however, in a sharp contrast to the concentrations in the underlying A horizon. This may be attributed to the rapid recirculation of its portion released from the decaying litter, as it is a major source of Mn in this otherwise highly Mn-depleted soil system. Even though the dominant form of Mn in the biological systems is Mn^{2+} with ionic potential in the range of low field strength elements, our results show little correlation between its behaviour and the behaviour of Fe, Rb, Sr, and Ba, with the highest value of Spearman's rank correlation coefficient being that of 0.31 for the correlation with Fe. Mobility of Mn must be therefore controlled by another mechanisms than those of low field strength elements.

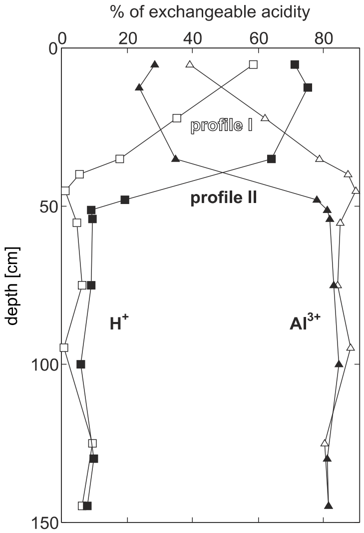


Fig. 4. Proportion of H^+ and Al^{3+} ion equivalents as a percentage of exchangeable acidity.

Table 3
Cation exchange capacity, exchangeable acidity, base saturation, pH, and organic C content of studied profiles.

a) Profile I

	CEC	EA	BS	pH_{H2O}	C
	cmol kg^{-1}	cmol kg^{-1}	%		%
A	6.50	6.19	4.7	3.69	10.0
E	0.66	0.63	4.9	4.60	0.2
Bhs	4.57	4.20	8.2	4.18	1.7
Bs	1.87	1.80	3.4	4.33	1.6
Bs/C	1.66	1.61	3.5	4.33	1.0
C1	2.22	2.12	4.2	4.38	0.8
C2	2.94	2.80	4.7	4.51	0.5
C3	3.42	3.18	7.0	4.70	0.4
C4	2.08	1.93	7.5	4.83	0.3
C5	2.42	2.23	7.8	4.97	0.2
C6	2.39	2.19	8.5	4.94	0.2

b) Profile II

	CEC	EA	BS	pH_{H2O}	C
	cmol kg^{-1}	cmol kg^{-1}	%		%
A	2.40	2.20	8.3	4.22	2.3
A/E	0.70	0.67	5.0	4.55	0.4
E	0.47	0.47	1.5	4.87	0.1
Bhs	4.61	4.28	7.2	4.45	2.0
Bs	3.56	3.40	4.4	4.38	1.4
Bs/C	2.00	1.92	4.0	4.38	0.7
C1	1.62	1.54	4.8	4.46	0.4
C2	1.78	1.66	6.6	4.92	0.2
C3	2.61	2.43	6.9	4.86	0.3
C4	2.51	2.31	7.8	4.92	0.2
C5	3.23	2.97	8.2	4.95	0.2

In order to evaluate factors that govern redistribution of studied elements in the course of podzolization, transitions of their concentrations upon the progression of podzolization front will be considered and patterns of light lanthanides characteristic for these transitions will be utilized as a possible tracers of pedogenetic processes. Light lanthanides from La to Gd have been chosen as they show higher rates of fractionation in comparison to heavy lanthanides and because both cerium and europium anomalies that are important for the interpretation of this fractionation may be observed in the range from La to Gd. Concentrations of light lanthanides in our soil show, upon the normalization to their average chondrite abundances, pattern typical for the upper continental crust. It is characterized by a gradual fractionation from light to heavy endmembers, with lanthanum being the most enriched, and by the distinct negative europium anomaly (Fig. 5). Even though all the horizons show this pattern, relations of elements in a particular horizon are unique and can be revealed by the normalization of concentrations to those in the material from which this horizon was derived.

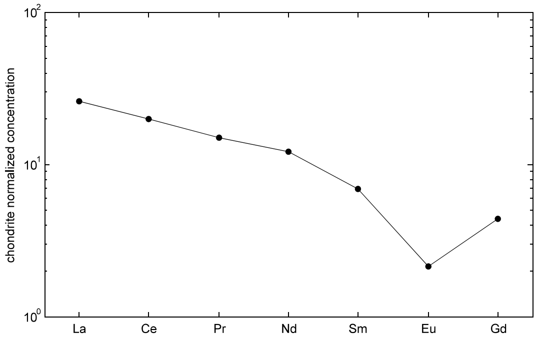


Fig. 5. Chondrite-normalized average concentrations of light lanthanides in both studied profiles. Normalization to CI chondrite abundances reported by McDonough and Sun, 1995 [17].

3.2 Transition from C to Bs horizon

Upon the transition of parent material to Bs horizon, apparent increase in the concentration of Fe occurs, that is being immobilized here by the precipitation in the form of (oxy)hydroxides (Fig. 6). Of all the studied elements, Fe is the most markedly affected by the redistribution due to a podzolization. Its illuviation indexes, given by the ratio of its concentrations in Bs to those in E horizon are 9.5 and 16.4 for profile I and II, respectively. Rb, Sr, and Ba are also being accumulated here, though in a lesser degree. Y and lanthanides show conservative behaviour in the acidic soil solution, with little fractionation taking place. Positive Eu anomaly is, however, apparent in Bs horizons of both profiles. This may be caused by the portion of Eu being present and transported in a reduced divalent state, behaving thus as a low field strength element. Its distribution is therefore closely related to these elements what is further evident from the principal component analysis (Fig. 7), as well as from the Spearman's rank correlation coefficients ranging from 0.73 for correlation with Rb, to 0.81 for that with Fe. Consequently, Eu shows the highest rates of uptake by plants and the lowest rates of overall leaching from the soil profiles of all light lanthanides.

In contrast to the behaviour of low field strength elements, Mn shows very little immobilization in the Bs horizon, indicating that its role in the podzolization is of a minor importance and that it is transported further downwards in the soil solution leaving the illuvial horizon. In the course of the downward percolation of soil solution, dissolved organic substances and elements that are bound to them may be immobilized and precipitated in the zones of the parent material that show a sharp decrease in the average particle size with higher content of silt and clay fractions. Sand deposits that serve as a parent material for our soils show a clear laminar texture with subhorizontal layers characterized by such sharp variations in the average size of mineral grains. As a consequence, thin Fe-rich bands form in the portions of C horizon where the texture is finest and permeability for the soil solution abruptly decreases.

Analysis of one of these bands that is situated between the C2 and C3 horizons of studied profile I, in the depth of approximately 90 cm, shows relative peak of exchangeable acidity with the value of 5.38 cmol kg^{-1}, as compared with the values obtained for underlying C3 horizon (3.18 cmol kg^{-1}) and the C2 horizon (2.80 cmol kg^{-1}) lying right above. Coupled with the relative peak of organic C content (1.0 %) and an abrupt change of base saturation from values lower than 5 % above the band to values higher than 7 % below, these data indicate that organic substances and elements bound to them are being removed from the percolating soil solution and immobilized in these zones. Upon the normalization to parent material (Fig. 8), obtained patterns are similar to those of Bs horizon, but show certain peculiarities. Concentration of Fe in the band is higher than those of Bhs and Bs horizons combined. This may be given by the fact that the finer structure of mineral matrix provides a higher specific surface area for adsorption of Fe phases, and also by the lower dilution effect resulting from the smaller size of matrix mineral grains than in the B horizons. Along with the Fe phases, Mn, Rb, Sr, Ba, and Eu are also being immobilized here, in contrast to Y and trivalent lanthanides that are being leached further downwards in the soil solution.

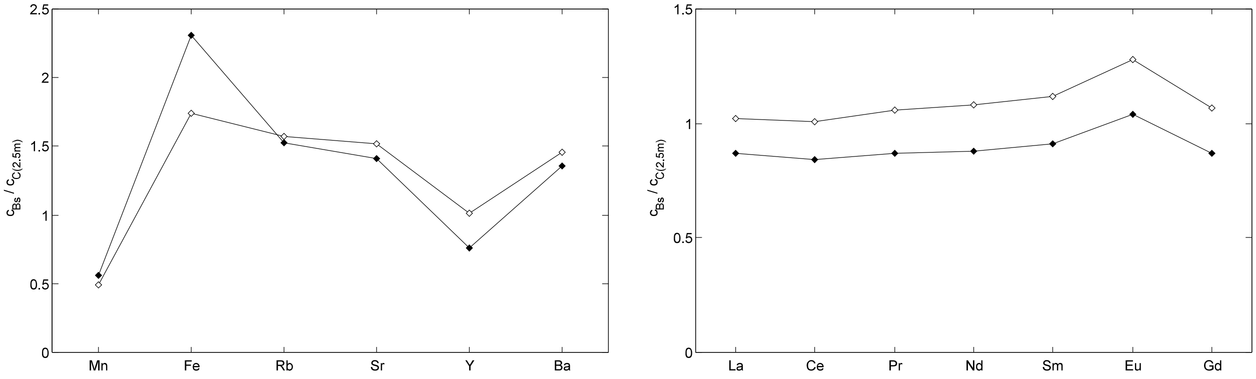


Fig. 6. Concentrations of studied elements in the Bs horizon normalized to average parent material composition.

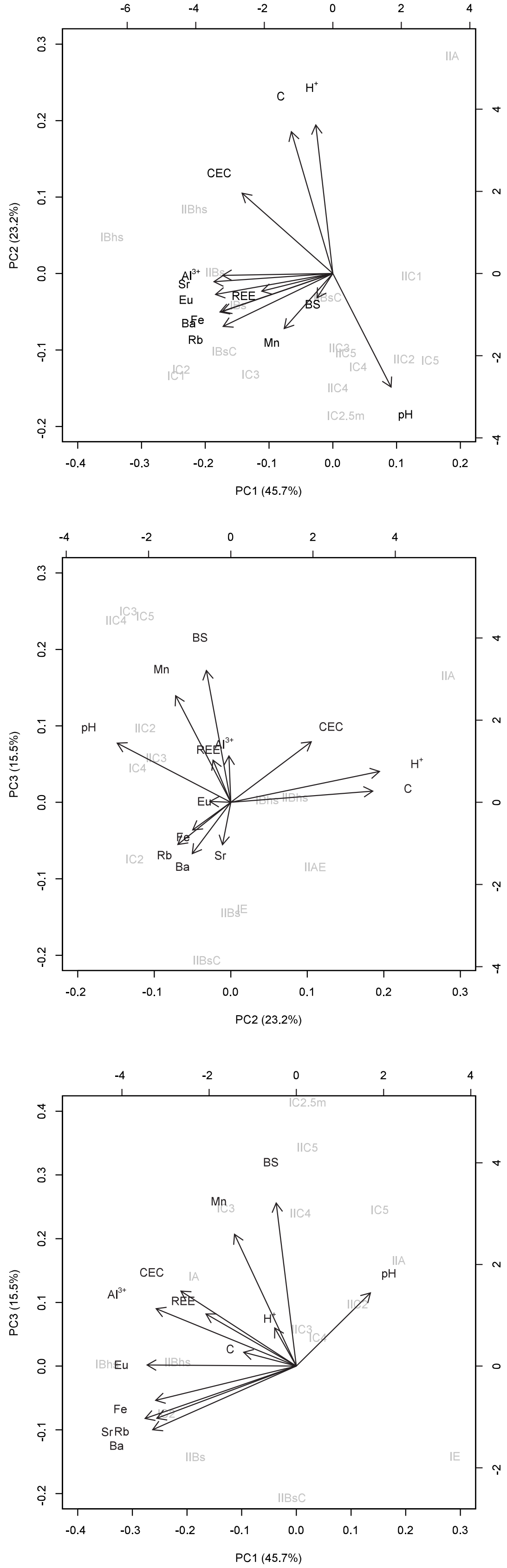


Fig. 7. Relations between the first three principal components accounting for 84.4 % of variability in bulk samples.

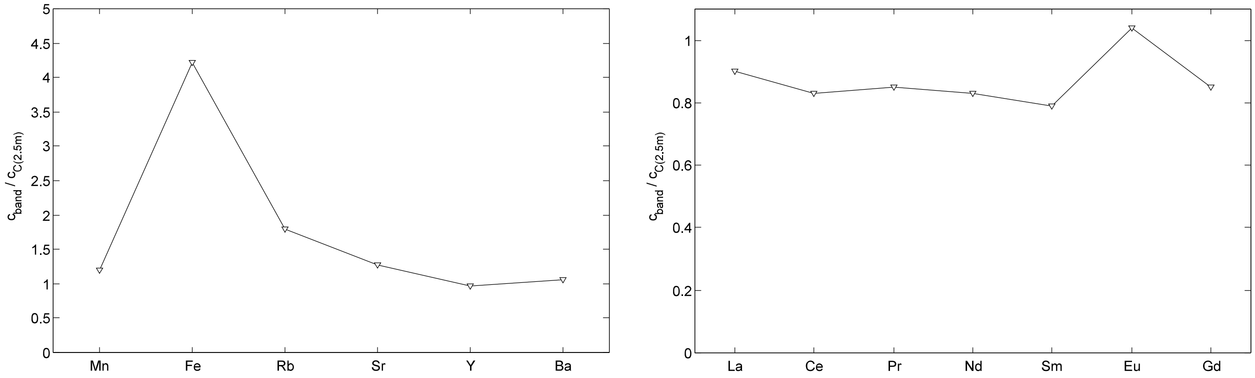


Fig. 8. Concentrations of studied elements in iron band normalized to average parent material composition.

3.3 Transition from Bs to Bhs horizon

Transition from Bs to Bhs horizon is accompanied by the progressive removal of Fe due to the action of organic substances dissolving its solid phases, while the overall contents of organic matter - either illuviated or root-derived - tend to increase. Bhs horizon is therefore characterized by the relative maxima of organic C content, as well as values of exchangeable acidity, base saturation, and consequently also Rb, Sr, and to a lesser extent Ba. Behaviour of Ba may be explained, as already noted, by its lower mobility in the course of weathering and additionally by the lower rates of uptake and subsequent recirculation by plants. While Y and lanthanide patterns still reveal low rates of fractionation, positive Eu anomaly is being preserved or even increases, suggesting that the organic matter plays an important role in its transport and immobilization. Content of organic C seems to be the key factor controlling the pH in the studied soils, with the value of Spearman's rank correlation coefficient between these variables being equal to -0.89. As a consequence, relatively sharp decrease in pH may be observed on the transition from E to Bhs horizon. This seems to be a characteristic feature of nutrient-poor intrazonal podzols, in contrast to boreal podzols, where pH tends to increase continuously with depth. As Bhs horizons of well-drained podzols have been found to contain higher portion of active roots, compared to those with lower permeability, an active exudation of protons and organic acids, apart from those illuviated from the topsoil, presumably induces this pH drop. While CEC and pH profiles of our soils seem to be in accordance with the data reported for podzols from heathlands of northern Germany [18], observed maxima of base saturation in the Bhs horizon contradict the minima found in German soils. This may be accounted for by the fact that while in our extremely nutrient-poor conditions organic matter serves as a relatively rich source of base cations, in a less nutrient depleted conditions of

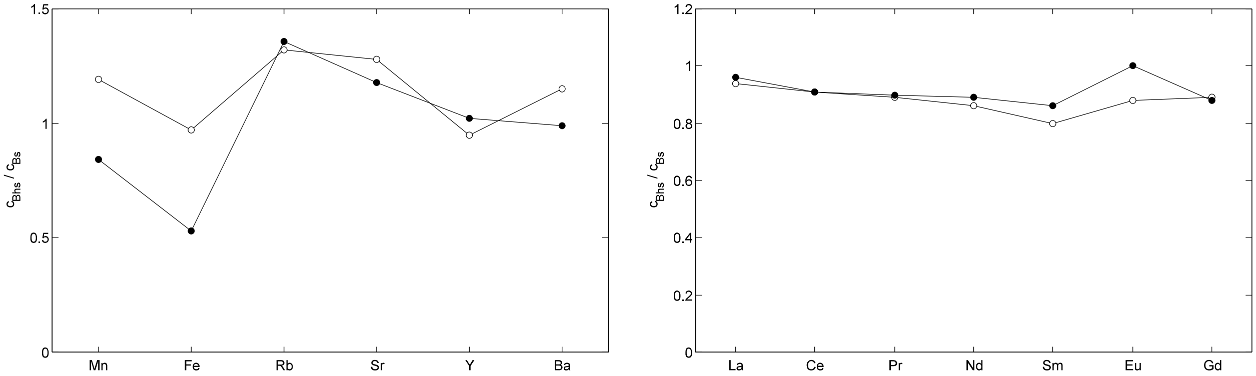


Fig. 9. Concentrations of studied elements in the Bhs horizon normalized to concentrations in the Bs horizon.

German soils, organic matter illuviated to the B horizon dilutes the overall concentrations of the base cations.

3.4 Transition from Bhs to E horizon

Final major shift in the composition of parent material during the progression of podzolization front is the removal of illuviated and root-derived organic matter from the interstitial spaces and further weathering of exposed mineral surfaces. As the E horizon is a source of the elements in the illuvial horizon, normalized patterns of its element concentrations (Fig. 10) show inverse character compared to those of B horizon, with all elements being depleted. Substantial negative Eu anomaly is of particular interest as the opposite trend is often observed in the course of weathering [3]. This is caused by the relative accumulation of feldspars, and mainly plagioclases that are highly enriched in Eu due to its substitution for Ca and Na in their structure. Only after the weathering proceeds further and plagioclases are destroyed - leaving in the residue only potassium feldspar that is not necessarily enriched in this element - sufficient amounts of Eu are mobilized and its relative anomalies may shift towards the negative range. As this is the case for eluvial horizon of our soils, it is evident that they represent an advanced stage of parent material weathering. Furthermore, the absence of Ce anomalies in the normalized patterns indicates that reducing conditions are not the governing mechanism in the eluvial-illuvial redistribution, as opposed to the podzols in the boreal region [19]. Occurrence of periodical short-term conditions of water-logging, however, cannot be completely ruled out on the basis of this observation, as binding to the organic ligands is known to cause a diminishing of the positive Ce anomalies in the solid phase [20, 21].

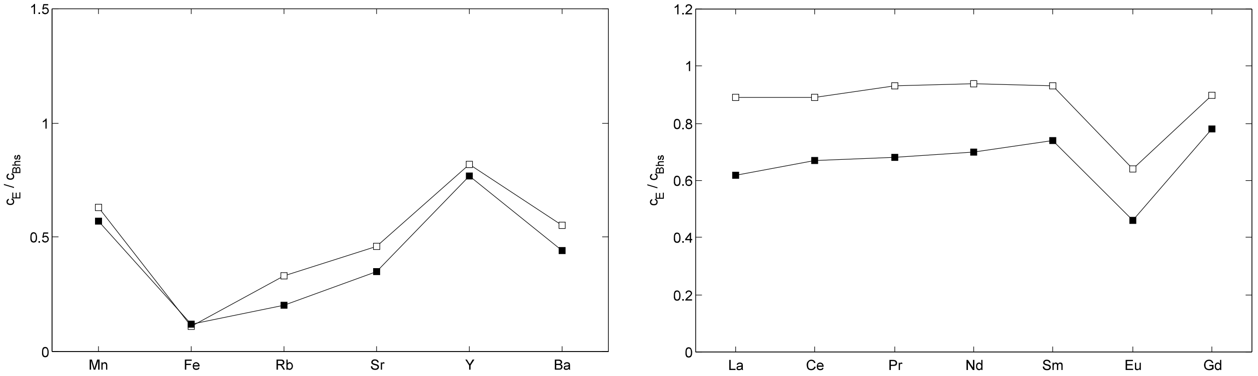


Fig. 10. Concentrations of studied elements in the E horizon normalized to concentrations in the Bhs horizon.

3.5 Micromorphology

Fig. 11 shows micromorphological characteristics of studied podzols observed in the thin sections of individual soil horizons. E horizon consists solely of mineral matrix represented by quartz and highly weathered feldspars (Fig. 11a,b), devoid of all interstitial organic matter except the still active fungal hyphae weathering the residual minerals. Markedly different is the situation upon the transition to Bhs horizon where most of the pores are clogged by the aggregates of polymorphic organic matter (Fig. 11c), often with the visible remains of plant tissues (Fig. 11d). This supports the notion that the majority of organic matter in the illuvial horizon is root-derived as opposed to the illuviated organic matter that characteristically forms monomorphic coatings on the mineral grains [22]. However, Fe phases further downwards in the Bs horizon form such a monomorphic coatings (Fig. 11e), indicating that the iron precipitating here is transported in the soil solution with the dissolved organic matter. Feldspars in this horizon (Fig. 11f) show considerably lower degree of weathering compared to those in the E horizon just a few centimetres above. Even though these

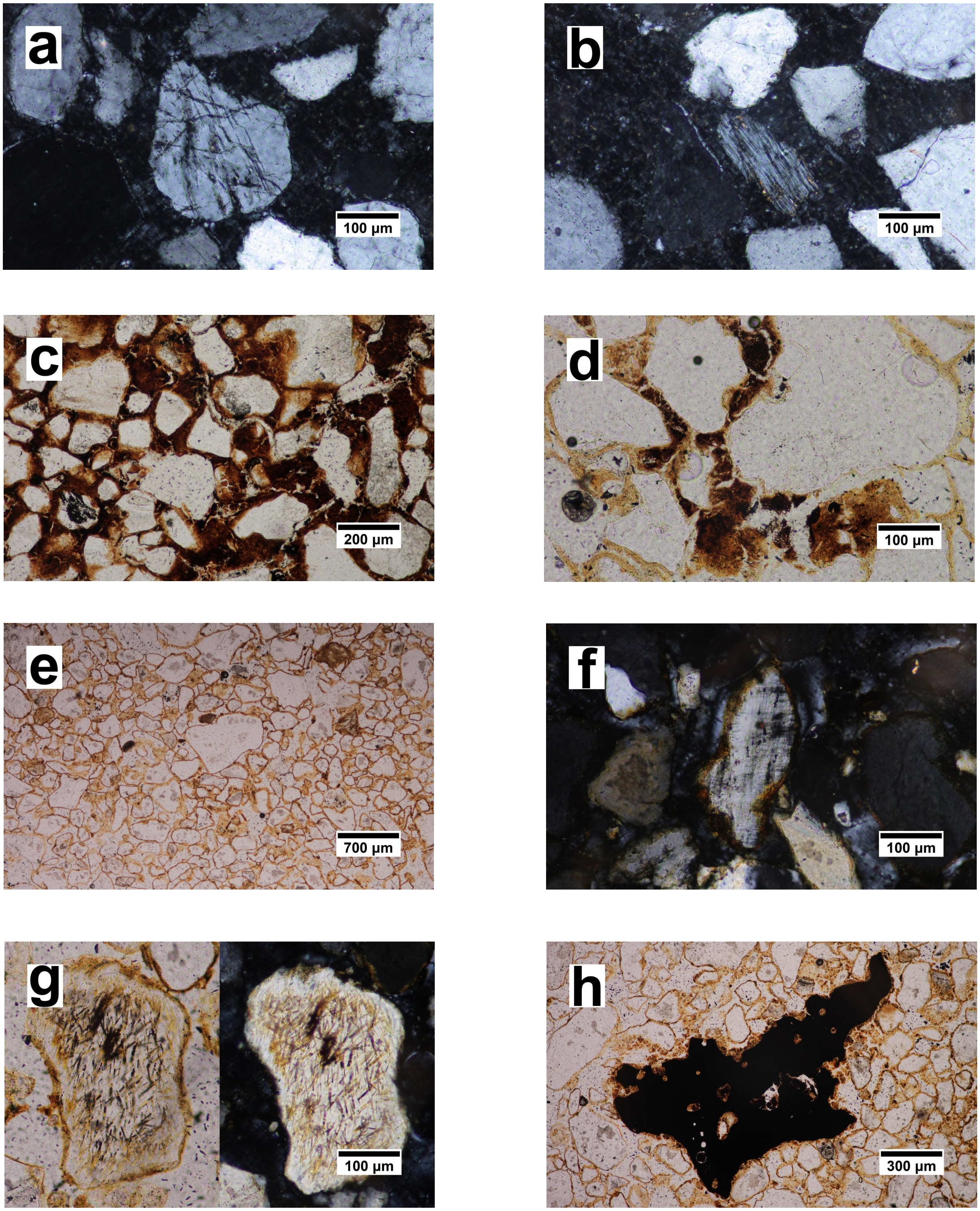


Fig. 11. Micromorphological characteristics of studied podzol. a, b) weathered feldspars in the E horizon (crossed polarizers); c) polymorphic organic matter in the Bhs horizon (plane-polarized light - PPL); d) visible remains of plant tissues in the Bhs hozion (PPL); e) monomorphic coatings of Fe solid phases in the Bs horizons (PPL); f) feldspar in the Bs horizon (crossed polarizers); g) mineral grain from the Bs horizon showing high degree of penetration (left - PPL, right - crossed polarizers); h) charcoal particle from the Bs horizon (PPL).

observations - and observations of other authors [23] - indicate that the rate of fungal tunnelling in the illuvial horizon is minimal, several mineral grains show an extensive degree of perforation (Fig. 11g). Whether this is a result of fungal activity is, however, uncertain.

Particles of charcoal (Fig. 11h) are present in all studied soil horizons, suggesting a frequent recurrence of fires. Anthracological study of this area [24] revealed that fires play an important role in the sustenance of local vegetation stability since at least the late Boreal, with the oldest charcoal sample dated to 6420 cal. BC.

4 Conclusions

Results of this work suggest that the major role of organic matter in the processes of podzolization may be more pronounced in the extremely nutrient-poor conditions where the predominant part of organic matter in the B horizon is root-derived and where presence of this organic matter substantially controls the pH values of the soil. Eluvial-illuvial redistribution was found to induce different mobilization rates of studied elements, the overall order being: Fe > Rb > Sr > Eu > Mn > light lanthanides > Y.

Even though the normalized patterns of light lanthanides show relatively low rates of fractionation due to their conservative behaviour in the acidic conditions of soil solution, they nevertheless indicate preferential illuviation of lighter members over the heavier ones, and the distinct europium anomalies further point to its different behaviour due to an increased mobility in the divalent state.

Lithology of the parent material plays an important role in the formation of studied podzols as its subhorizontal laminar texture favours the removal of the elements and organic matter from the soil solution and their accummulation on the sharp textural boundaries in the C horizon, giving rise to a thin pans cemented predominantly by the Fe solid phases. When progressing podzolization front reaches one of this pans, its downward movement is expected to decrease, and the material of the iron pan is incorporated into the B horizon, leading to an increase of cementation and a higher contrast of its composition as compared to the eluvial horizon.

Comparison of studied profiles shows that the mean depth of illuvial horizon of profile II, as well as content of organic carbon in this horizon and overall degree of illuviation of all the studied elements is higher than that in the profile I. Thus, if we assume that the profile II represents a more developed podzol than profile I, comparison of the concentrations of elements normalized to their average parent material contents reveals the trend of increasing divergence of the composition of eluvial and illuvial horizon in the course of podzolization, while at the same time the overall depletion of elements in a weathering profile takes place with increasing age.

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