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Metals in 1–0.25 mm grain-size fraction in the soils of the mixed forest zone of the Russian plain

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ABSTRACT

For an improved understanding of metal behavior in soils, studies on geochemical changes occurring in a specific grain-size fraction during pedogenesis and lateral translocation of soil material are needed. In the present research we analyzed the concentrations and vertical distributions of Fe, Mn, Cu, Ni, Co, Cr, Zn, Pb, Ti, Zr in coarse and medium sand fraction of the major soil types of the middle Protva basin, situated in the mixed forest zone of European Russia, and described patterns of downslope (lateral) distribution of metals in the humus horizons along two catenas and two types of small erosional systems. The observed concentrations for all metals in the fraction 1–0.25 mm, except of Mn, conform to the natural geogenic concentrations reported previously in literature. The majority of the metals exhibit high natural variability in concentrations in the sand fraction. Higher metal concentrations are found either in the topsoil horizons or in parent material and underlying stratum. Studying lateral aspects of metal distribution in the sand fraction of humus horizons revealed a decrease in Mn, Zn, Pb, Co, Ti and an increase in Fe, Cr and Ni levels of the lower sections of the slopes. The similarity of metal concentrations in the sand fraction in these positions across two catenas implies the importance of the geochemical convergence processes operating in downslope direction. The small erosional landforms, a gully and a dry U-shaped valley, show similar patterns in lateral distribution of Fe, Cu, Ni, Cr, Zr, Zn, but they differ in terms of Pb, Co and Mn behavior across their elementary units: adjacent areas, slopes and bottom. The results imply that the features of vertical (within the soil profiles) and lateral (along catenas and small erosional systems) distributions of metals are significantly controlled by the provenance of the sand fraction, although at the same time some variations in metal contents seem are attributed to chemical transformations of the sand fraction due to pedogenic processes and during downslope translocation of soil material.

1. Introduction

Potentially hazardous metals occur in unpolluted soils in a number of different chemical forms, which means that their fate in the environment should differ (Hardy and Cornu, 2006). Lithological and geochemical features of parent material together with site-specific geochemical conditions and pedogenic processes influence the types of elements' occurrence and their bonding to certain phases. Simple measurement of total metal concentrations in soils is commonly used to detect the cumulative effect of various factors but does not give any indication of specific behavior of the metals necessary for better understanding of their fate in the environment. A shift to more sophisticated fractionation-based approaches, which took place several decades ago both in applied and fundamental studies, was intended to increase the knowledge about the complex nature of metals' occurrence and their pathways in the environment. Sequential extraction of metals from solid media is a common analytical tool which is widely used in environmental and exploration geochemistry. It is applied to evaluate the mobility of metals and classify them according to their affinity to operationally defined geochemical fractions (Pagnanelli et al., 2004; Sutherland and Tack, 2003). Physical fractionation, based on particle size, allows separating a bulk soil sample into certain solid phases (sand, silt and clay). Each of these fractions imparts its own character to the soil and has distinct properties (Brady and Weil, 1999). The division of fine earth material according to the particle sizes is of considerable interest because various soil particle groups participate differently in a number of soil and geochemical processes, including vertical translocation through soil profiles and also physical migration due to wind and water erosion. It is well known that the distribution of metals is dependent on particle sizes and reflects mineral fractionation across grain sizes. Acosta et al. (2011) have shown that the type of rock is the major factor defining trace element contents in different particle-size groups, however some variations might occur in soils due to weathering, formation of secondary Fe-oxides, elemental fixation and other pedogenic

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processes. Many studies report (Acosta et al., 2011; Acosta et al., 2009; Pagnanelli et al., 2004) that finer soil material has a higher ability to carry heavy metals than coarser fractions because of larger specific surface area, the enrichment with organic matter and higher amounts of Fe, Mn, Al oxides and hydroxides (Acosta et al., 2011; Förstner, 1982; Huang et al., 2014; Xu et al., 2013). This explains why the studies on metal variability in soils and soil systems focus mainly on finer fractions (Acosta et al., 2011; Plyaskina and Ladonin, 2005; Pobedintseva, 1975) while the importance of soil sand geochemistry is neglected. Coarser fractions, especially sand, in most cases, is considered to be more geochemically inert among other particle groups, however sand particles might contain geochemically active phases and under certain conditions be involved in translocation processes at a landscape level. Moreover, there are many areas with coarse textured parent materials and underlying lithologies, where sand, being the major mineral constituent of the soil solid phase, represents an important participant in soil formation. The understanding how trace elements contents vary along soil systems in the coarser fractions is one step towards assessing their role in the spatial geochemical heterogeneity of the soil cover.

The objective of this study was to identify geochemical variations and trends in geochemical transformation of the coarse and medium sand fraction (1–0.25 mm) in relation to pedogenic processes and downslope (lateral) migration along soil sequences in the mixed forest zone of European Russia. The choice of the grain-size fraction was based on the results of our previous works concerning soil geochemistry of the study area (Samonova et al., 2013) where we examined metal concentrations in different grain-size fractions and assessed the effect of particle sizes on metal distribution. Our results confirmed that the accumulation of metals preferentially takes place in the finest fraction (< 0.001 mm) however it was also revealed that some metals tend to be associated with coarser particle size, for example silt (Ti, Zr). A wide range of elements (Mn, Co, Ni, Cr, Fe) enriched the clay fraction but also showed the second maximum in the coarse and medium sand fraction. The results of mineralogical analysis carried for the study area (Rychagov and Antonov, 1992) suggest that these elements might be present in geochemically active compounds since this soil sand fraction contains a lot of newly formed Fe- and Mn oxides and hydroxides. The elevated concentrations of a wide range of metals, which are probably present in a potentially mobile form, indicate that this fraction might provide a significant contribution to the total metal concentrations of bulk samples and therefore is important enough to be included in soil geochemistry studies. To see the effect of soil formation we analyzed concentrations and vertical distributions of metals associated with the coarse and medium sand fraction in the major soil types of the study area. To infer the effects of downslope processes we researched the patterns of the lateral distribution of the metals in this fraction for the surface horizons of two catenary systems and two different types of small erosional landforms present in the study area (a gully and a dry “U” shaped valley, called *balka* in Russian). It was hypothesized that comparing the sand fraction in soils of two different erosional landforms will reveal not only the difference in the metal contents because the landforms belong to different lithological types but also similar trends in lateral changes of the metal concentrations because the migration of sand particles and their transformation during lateral migration takes place under same bioclimatic conditions.

2. Materials and methods

2.1. Description of the study area

For the geochemical study presented here we chose the area near the Moscow University research station Satino, where detailed geological survey, geomorphological mapping, investigations on soil erosion and gully erosional rates, studies on soils and vegetation cover have been conducted during the last 40 years (Antonov et al., 2001).

The study area is located in the middle part of the river Protva basin, 100 km to the southwest from Moscow (Fig. 1), in Smolensko-Moskovskaya Upland (314 m ASL). Climate of the study area is humid temperate continental, characterized by moderately moist and warm summers (T July = 17.5 °C) and cold winters (mean T January = − 9.9 °C), and mean annual precipitation about 600 mm. The present-day morphology of the study area is characterized by glacial relief on interfluves of Moscow (MIS 6) age, corresponding to the Saale III stage of the Saale glaciation in West European glacial regions (Velichko et al., 2011), and post-Moscow fluvial relief of river valleys and gullies.

Major glacial features of the topography were formed during the Middle Pleistocene glaciations (the Dnieper, MIS 8 and the Moscow, MIS 6). Several layers of glacial tills, glaciofluvial sands and silts were deposited over pre-Quaternary bedrock − Carboniferous limestones and dolomites. The following deglaciation caused the incision of the Protva river and the related increase in topography range. High surface runoff erosion during this period created a network of slope hollows. Such forms were much smaller than the glaciofluvial depressions formed by meltwaters in periglacial environment during the Moscow age glacier degradation. During the Late Pleistocene the area was not glaciated and several incision-aggradation cycles of the fluvial network occurred. Periglacial conditions related to Valdai (Vistulian, MIS 2–4) cold epoch had profound effect on the landscape formation in the study area. The main tendency during this period was the infilling of the existing depressions (both large and small hollows) with colluvial sediments due to a complex action of solifluction and gelifluction processes (Eremenko et al., 2010; Panin et al., 2009). The increasing aridity during this cold epoch was accompanied by a deposition of a 2–3 m thick layer of the loess-like carbonate-free mantle loam which covered all types of Quaternary (glacial and glaciofluvial) sediments in hollows, interfluves and upper river terraces (Rychagov and Antonov, 1996; Panin et al., 2009). Various textures formed by flow-like mass movement can be observed both in the mantle loams and underlying deposits. Soon after degradation of the periglacial environment, many of the depressions began to be dissected by the new-forming erosional landforms which inherited existing catchments.

Modification of the morainic topography by postglacial processes and mass movements during last 150 kyr, resulted in the smoothed relief features: the majority (95%) of the area is $< 5^\circ$ steep (Panin et al., 2011). Most morphological elements of the interfluve areas, such as moraine hill tops, glaciofluvial hollows and sandurs, constitute subhorizontal surfaces with angles $< 2^\circ$ (Fig. 1). The steepest topographical elements in the study area are the sides of the river valleys. They are dissected by a number of gullies 5–15 m deep. The headcuts of the gullies often penetrate into interfluve areas, while their fans overlie floodplains or protrude directly into the river channel (Fig. 1).

Gullies cut through various types of rocks and their development is considered to be under the control of available catchment areas as well as geomorphic and lithological properties of valley sides (Panin et al., 2011). According to the lithological units that prevail in the vertical sections, all gullies in the study area represent three lithological types: bedrock gullies, till gullies and sand gullies (Belyaev et al., 2005; Panin et al., 2009). The most common are till gullies with smooth longitudinal profile.

According to the morphological differences and some stratigraphic evidences and dates (Panin et al., 2009; Belyaev et al., 2005), two generations of gully origin can be distinguished in the study area – Pleistocene gullies and Holocene gullies.

Pleistocene gullies (termed *balka* in Russian if they are dry U-shaped valleys) constitute the majority of the gullies. Most of the Pleistocene gullies belong to the “till” type – they cut through tills with less involvement of glaciofluvial sands. During the Late Valday cold epoch (MIS-2) (Panin et al., 2009), they had a hollow-like morphology. At the next stage, which took place in the Late Glacial, due to the increased surface runoff, there was an incision of steep V-shaped gullies into more gentle and older landforms (Panin et al., 2009). The subsequent

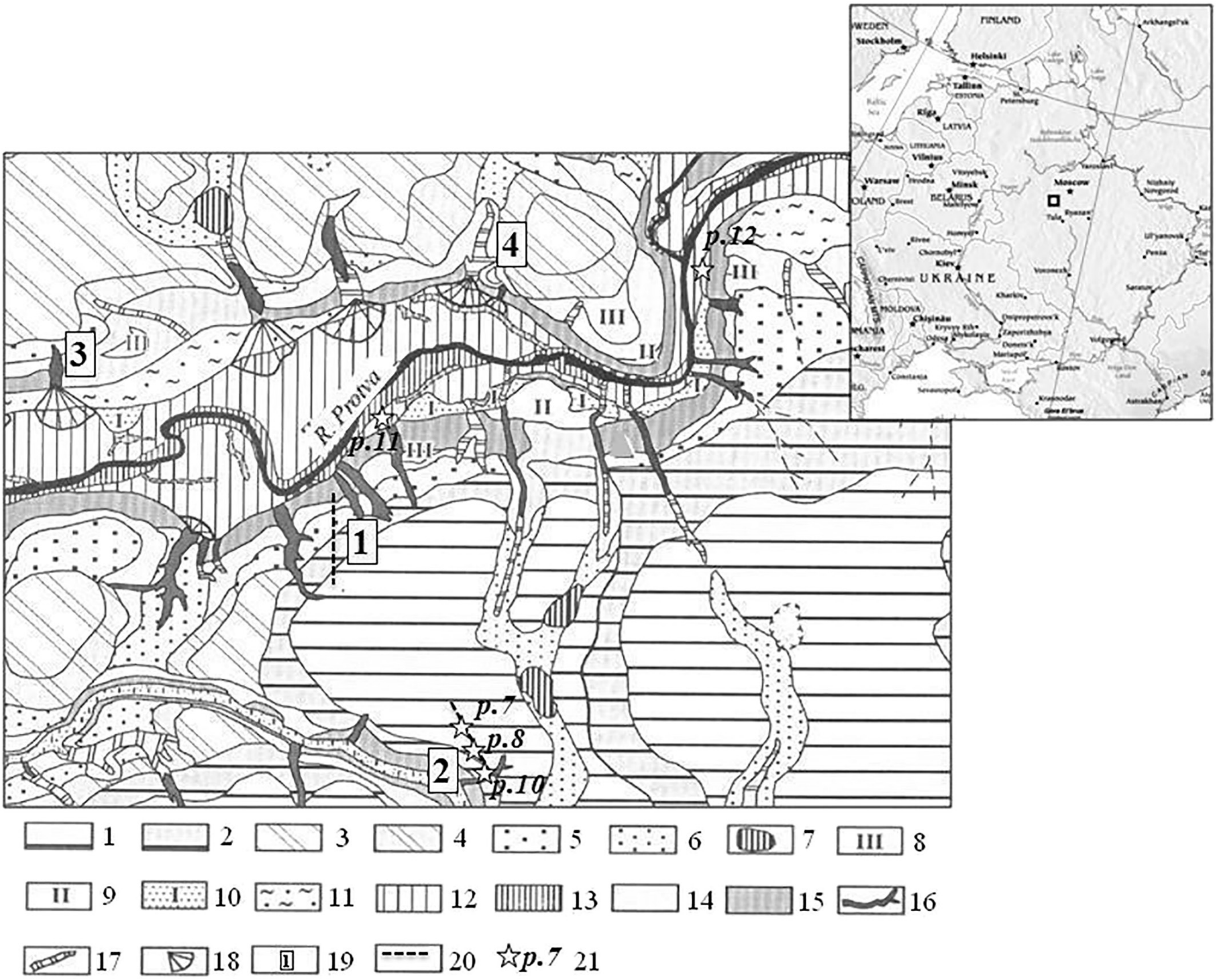

Fig. 1. Geomorphic map of the study area (modified after Antonov et al., 2001) with locations of the study objects.

Glacial and glaciofluvial landforms of the Moscow glaciations (MIS 6) modified by later processes: 1,2,3,4 – sub-horizontal surfaces and gentle slopes of moraine hill tops with Quaternary cover thickness ≤ 25 m (1, 2) and ≥ 25 m (3, 4). The surface deposits are represented by mantle loam and diluvium underlain by glacial till and glaciofluvial sands; 5 – sub-horizontal surfaces of the valley sandurs. The surface deposits are represented by mantle loam underlain by glaciofluvial sands and ancient alluvial stony sands; 6, 7 – sub-horizontal surfaces and gentle slopes of glaciofluvial hollows (6) with former lake bottoms inside those (7). The surface deposits of glaciofluvial hollows are represented by mantle loam underlain by washed till, glaciofluvial sands and silts. The former lake bottoms are composed of glacio-lacustrine deposits (loam, silt and sand).

Fluvial landforms of late and post-Moscow age: 8 – Late Moscow terrace (MIS 6) composed of shallow mantle loam and deluvium, underlain by washed till, glaciofluvial sands and ancient alluvial stony sands; 9 – Early Valday terrace (MIS 4), 10 – Late Valday terrace (MIS 2). The Early and Late Valday terraces are mainly composed of loamy deluvium underlain by alluvial stony sands, till and glaciofluvial sediments; 11 – alluvial terraces smoothed by mass movement processes (slopes over former terraces). The surface deposits are represented by loamy diluvium; 12 – high floodplain composed of alluvial loams underlain by sandy deposits; 13 − lower floodplain levels with sandy sediments and weakly developed varieties of fluvial soils; 14, 15 – erosional slopes < 5° (14) and > 5° (15). The surface deposits are represented by diluvium which is underlain by various deposits; 16 – gullies; 17 – balkas; 18 – gullies' detrital fans.

Other marks: 19 – study objects: catenas (1, 2) small erosional landforms (3, 4); 20 – location of the soil catenas; 21 – representative soil profiles and their number codes.

development of the Pleistocene gullies continued in the Holocene during phases and episodes of high erosion. The low-erosion periods resulted in the accumulation of sediments in the gullies bottoms.

The gullies formed in the Holocene are V-shaped. Compared to the Pleistocene ones, they are smaller in length (100–230 m versus 270–900 m) and catchment area (1.7–7.2 versus 9.7–63 ha). They are only 4 gullies of this type in the study area. All Holocene gullies are cut into the rather steep slopes (> 15°) which are composed mainly of highly erodible glaciofluvial sands and silts. Usually no to very little sediment storages are found in their bottoms. According to Belyaev et al. (2005) and Panin et al. (2009; 2011) the initiation of these gullies occurred in second half of the Holocene between 5900 and 3000 years BP. The rise of gully erosion coincided with climatic changes and increased strength of extreme weather conditions while human impact on erosion was minimal to absent. Erosional effects produced at that time according to Panin et al. (2011) have no analogs in the Holocene. Radiocarbon dating shows that the following erosional peaks in gully deposits also revealed the correlation with climatic signals (Panin et al., 2011).

The human contribution to the erosion/sedimentation dynamics in the study area is believed to have started only in the 14th–16th centuries AD (Antonov et al., 2005; Panin et al., 2011). The most severe forest clearance in the study area took place in the mid-18th century. During that time only 7% of the area was forested while arable lands occupied 67% (Antonov et al., 2005; Panin et al., 2011). Today the area of cultivated lands has dropped to 37% and the area under natural vegetation has grown up to 42% (Antonov et al., 2001). Modern land cultivation promoted the increase of sheet erosion on arable hillslopes, however the evidences of linear erosion development in the study area are not so widespread. Recently, gully erosion accounts for only 6% of the total sediment load (Golosov, 1996). The results of studies on sediment budget for the central parts of the Russian plain (Golosov, 2006a, b; Belyaev et al., 2009) show that soil material mobilized from arable hillslopes is deposited before reaching the river channels.

The soil cover of interfluves is dominated by Retisols (IUSS Working Group WRB, 2015). In the Russian classification system these soils correspond to sod-podzolic soils, which develop mostly on mantle loam under mixed forest (oak-spruce, lime-spruce, birch-spruce) vegetation. They are characterized by a medium humus content. In the study area these soils occupy sub-horizontal surfaces and gentle slopes of moraine hills and valley sandurs. About 50% of these soils were subjected to arable farming, mostly on the left bank of the river Protva. Gleyic varieties of sod-podzolic soils are characteristic of the flat bottoms of glaciofluvial hollows, dissecting the interfluve areas. These relatively poorly drained lands are occupied by natural small-leaved forest and mixed vegetation and used mostly as pastures. Soils with two-stage profiles, formed in non-uniform parent materials, can be also found in the interfluve areas but their occurrence is limited to sites with shallow mantle loam cover. The Protva valley bottom is represented mostly by a floodplain zone with fluvial calcaric loamy soils which are intensively used in arable and pastoral farming. Alluvial terraces with sod-podzolic soils occupy limited areas in the Protva river valley bottom. Historically, they were the sites where the earliest arable farming and settling started. In contrast to these landscapes, very little anthropogenic impact have been observed on steep valley sides and in gullies, zones dominated by Regosols (IUSS Working Group WRB, 2015) and covered by natural meadow, mixed forest or broadleaf (oak-lime) forest vegetation. The soils in these landscape positions have a weakly developed profile, sometimes exhibiting calcaric features, and are classified as soddy soils in the Russian classification. Similar soils with buried soil horizons are found usually in depositional footslope positions.

Mineralogical and major chemical features, as well as textural differentiation, of sod-podzolic soils of the center of the Russian Plain were investigated in detail by Tonkonogov et al. (1987), while the distributions of total metal concentrations in the soil systems and parent materials of the study area were examined by Kasimov et al. (2003) and Samonova and Aseyeva (2006).

2.2. Study objects and soil sampling

The objects selected for the analysis included: 1) representative soil profiles to examine vertical geochemical differentiation in the sand fraction; 2) surface A horizons of two catenas and surface horizons of two small erosional landforms, in order to study spatial aspects in metals distributions (Fig. 1).

The locations of the studied soil profiles are displayed on Fig. 1. The first soil profile (p. 7, Fig. 1), the sod-podzolic soil on mantle loam, occupied the gentle upper segment of the morainic hillslope. The second (p. 8, Fig. 1), a poorly differentiated soddy soil, was located in the steeper section of the slope and the third, a soddy gleyic soil (p. 10, Fig. 1), was formed in the bottom of a small gully. The other two soil profiles were located in the bottom of the main river valley: one soil (with recent AC profile and buried horizons) was developed on a gully's fan deposits (p. 11, Fig. 1), and another one (representing a calcareous fluvial soil, p. 12, Fig. 1) on loamy alluvial sediments in the central part of the floodplain. Sampling of the representative soil profiles required horizon type identification and was performed from the middle of the horizons. In total 21 samples from 5 soil profiles were collected.

In studying the spatial variation of the sand fraction geochemistry we used only A-horizon samples. Since the soil formation in the study area started after the Moscow (MIS 6) glaciation it is believed that the majority of the soils with AEBC profile have a polygenetic profile and long history of the development. A-horizon characteristics are essential in evaluating the more recent migration processes. In contrast, B-horizon properties could be used to suggest longer-term processes because, relative to the A-horizon, many of the properties of the B-horizon take longer to form.

The samples of surface A-horizons were collected from selected positions along two catenas and across various units of two erosional landforms – their slopes, bottoms, detrital fans as well as from adjacent areas considered as sources of solid material (Samonova et al., 2014).

The two catenas which were chosen for the analysis of the downslope migration of chemical elements were located under natural forest vegetation on the right bank of the Protva river where human inferences are minimal. Both catenas were located at higher elevations of the relief and comprised all segments of the two major geomorphic surfaces: their upper parts included typical soils forming on the smoothed interfluves with glacial/glaciofluvial relief. The soils of the lowermost positions characterized post-glacial surfaces created by erosion: the Protva river valley side (*catena* 1) and a small gully's slope and bottom (*catena* 2). In terms of lithologic and soil conditions in the study area, the selected soil sequences included soil types and parent materials of the widest occurrences (sod-podzolic, soddy, soddy gleyic soils forming on mantle loam and deluvium). Being forested and, thus, relatively stable in terms of recent sheet erosion and solifluction processes, the catenas represented predictable soil sequences, much of the variation in their soil cover was a function of relief since the parent material along the most parts of the catenas was rather similar. It was mostly represented by mantle loam and associated deluvium deposits. At the same time the lithologies of the selected catenas were not identical in terms of the depth and the genesis of the underlying strata (glacial or glaciofluvial), which might impact soil formation and vegetation cover. The textural features of the parent material and underlying rocks along *catena* 2 indicate the presence of glaciofluvial sands infilling a periphery of a glaciofluvial hollow buried under the shallow cover of loess-like loam. In contrast, in *catena* 1 the mantle loam cover is much thicker and the underlying strata is mostly dominated by till. Thus, in the view of underlying lithologies and the thickness of loessial deposits, the selected catenas reflect two different but very common for the marginal zone of the Moscow (MIS 6) glaciation lithological situations (Rychagov and Antonov, 1996). The catenas characteristics (their soil and vegetation cover, parent materials, underlying lithologies and sampling positions) are displayed in Fig. 2 and will be discussed later in more details.

We also included small erosional landforms in the spatial analysis, which play an important role in sediment transfer processes and are the common relief features of the study area. The selected systems, a Holocene gully and a Pleistocene *balka* (Fig. 3), belonged to two different types different in morphology, history and lithology. The gully is a smaller and younger system with a concave form of longitudinal profile and a cross-section represented mostly by a "V" shaped form. Its catchment area is only 17,000 m^2. Upper parts of the gully are incised into a rather thin layer of the Late Pleistocene loessial (mantle) loam which contains a lot of silt but higher proportion of clay than typical loess. Subsequently the landform cuts mostly through glaciofluvial sands and silts, with only limited involvement of boulder clays (the Moscow till in the upper reaches and the Dnieper till near the mouth). The soil cover of the gully's catchment is dominated by sod-podzolic soils under forest communities while in the bottom and on the slopes of the landform soddy soils and soils with weakly developed horizons under grass and large shrub vegetation are common (Gerasimova and Isachenkova, 2003). The gully's detrital fan is occupied by soddy soils with a relatively thick humus horizon developing under herbaceous meadow communities.

The *balka* is an older and a larger landform (with a catchment area of 328,000 m^2) incised mainly in till with less involvement of glaciofluvial sands. Its length is about 400 m, twice the length of the gully (Fig. 3). The large proportion of the catchment area is used as tillage.

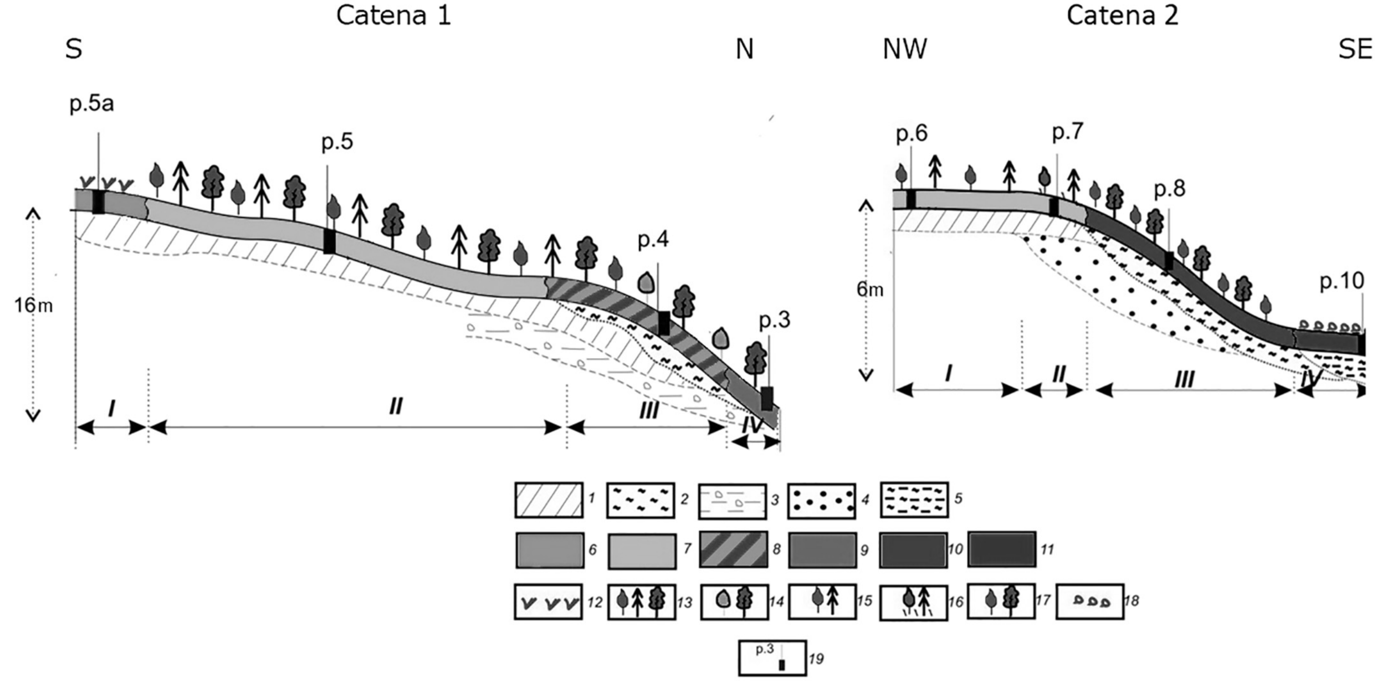

Fig. 2. The studied soil catenas. Catenary positions (I-IV): I –summit positions; II – III slope positions; IV – footslope and toeslope positions; Quaternary deposits (1–5): 1 – mantle loam, 2 – loamy deluvium; 3 – calcareous till; 4 – glaciofluvial sand; 5 – loamy deluvium and proluvium; Soils (6–11): 6 – sod-podzolic soils, ploughed in the past; 7 – sod-podzolic soils; 8 – soddy soils with buried horizons of sod-podzolic soils; 9 – soddy soils with calcaric subsoil; 10 – soddy soils; 11 – soddy gleyic soils; Vegetation (12–18): 12 – meadow; 13 – spruce-oak-birch forest; 14 – oak-lime forest; 15 – birch-spruce forest; 16 – aspen-spruce forest; 17 – birch-oak forest; 18 – forest herbaceous community; 19 – sampling locations and soil names and number codes.

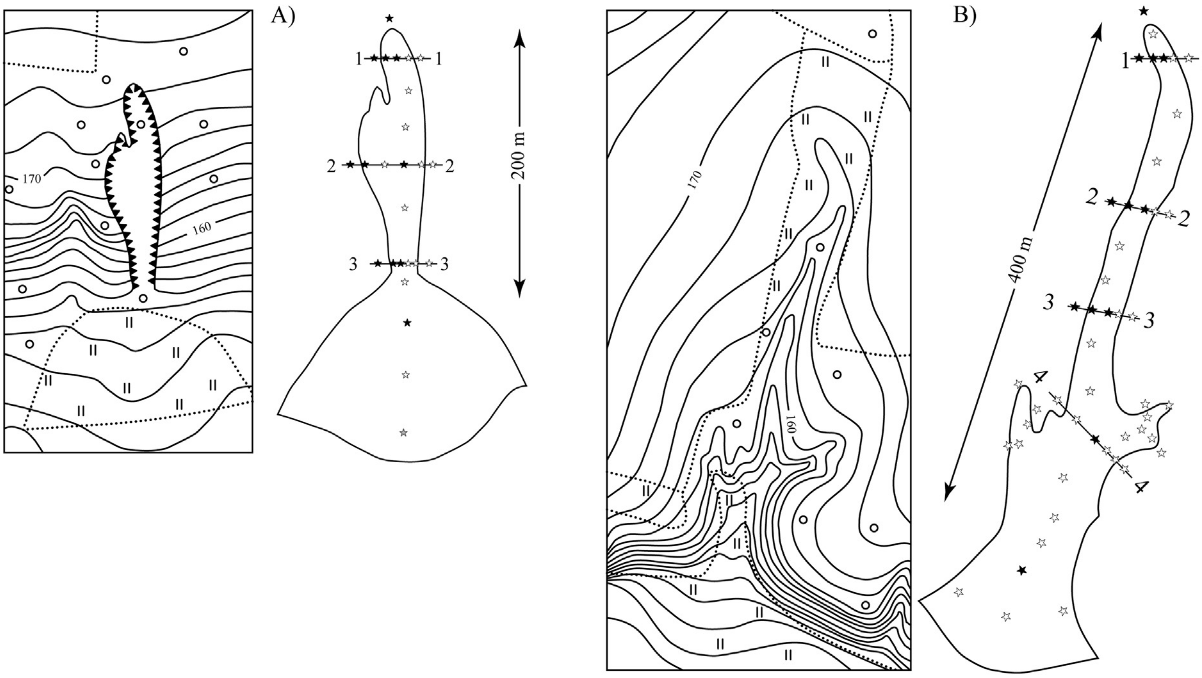

Fig. 3. The schemes of the gully (A) and the *balka* (B) with sampling locations. The contour lines interval on the topographic map is 2 m. The sampling locations in the schemes are indicated with five-pointed stars, cross sections – with Arabic numerals. Black stars indicate the positions where the concentrations of metals were measured not only in a bulk soil sample but also in the separated 1–0.25 mm grain-size fraction.

The soils of the *balka's* slopes and bottom are formed on loamy deposits and represent less sandy varieties found in the gully.

The soil samples were taken in the various units of these 2 systems from the uppermost soil horizons (0–10 cm) according to the scheme, presented in Fig. 3[1]. Overall, 23 soil samples were selected for the physical fractionation.

2.3. Analysis

All collected soil samples were air-dried and crushed to pass through a 1-mm mesh sieve. The bulk samples were analyzed for the content of the organic matter using $K_2Cr_2O_7$ wet-combustion method (Arinushkina, 1992) and exchangeable soil acidity in a 1 M KCl suspension (Vorob'eva and Avdon'kin, 2006). Particle size analysis was performed after pretreatment of the samples with sodium pyrophosphate (Arinushkina, 1992) without previous H_2O_2 oxidation of organic matter. The sand fraction was separated by sieving while the fractions 0.05–0.01 mm; 0.01–0.005 mm; 0.005–0.001 mm (coarse, medium, fine silt, respectively) and < 0.001 mm (clay) were determined by the pipette method.

In the separated coarse and medium sand fraction (3–4 g) the concentrations of Mn, Cu, Ni, Co, Cr, Zn, Pb, Ti, Zr were determined by atomic emission spectroscopy with 3-phase dc arc using DFS-458 equipment, while the concentrations of Fe were determined by atomic absorption spectrometry. The average precision of the analyses was generally within 10%. In total 49 samples of the sand fraction, 35 of which were obtained from A horizons, were analyzed.

2.4. Data treatment

The data treatment included the calculation of descriptive statistics and correlation matrices, using the software program SPSS v11.0. Average values of the parameters were calculated as arithmetic means and medians. The relationships between elements were evaluated using Pearson's correlation coefficient and significance level of 0.05.

To obtain a better understanding of the distribution of the metals in the sand fraction of the soil profiles, we estimated the values of a transfer factor TF, which enhances variations in their concentrations across soil horizons with respect to the parent material using the following formula:

$$TF = X_i/X_p$$

where X_i is the metal concentration in the sand fraction of a genetic horizon of a given soil and X_p is the metal concentration in the sand fraction separated from the parent material. Values of 1.0 indicate that the metal content in the sand fraction of certain soil horizon is the same as in the parent material, values > 1.0 indicate the enrichment relative to the parent materials, while values < 0.1 imply relative depletion or loss of metals due to pedogenic processes.

Geochemical changes along the catenas' positions and across the various units of the small erosional systems were evaluated using the L coefficients. According to Glazovskaya (2002), in the catenary analysis the L coefficient quantifies the geochemical differences between soils of summit positions (which are used as reference site) and subordinate landscapes in the lower parts of a *catena*. The following formula was used:

$$L = X_i/X_{Su}$$

where X_i is the metal concentration in the sand fraction of a given catenary position, and X_{Su} is the metal concentration in the sand fraction in soils of the summit position.

For the erosional landforms this coefficient was calculated by estimating average concentrations of the metal in the sand fraction for each unit and rescaling them relative to the average metal concentration in sand fraction in the reference position (which was the adjacent area unit) according to the following formula:

$$L = X_c/X_{AA}$$

where X_{AA} was average metal concentration in the sand fraction of the reference unit, i.e. the adjacent area, and X_c was the average metal concentration in the sand fraction of a particular landform unit, i.e. slopes, bottom or fan.

The axial distributions of metals in the longitudinal sequences of soils were analyzed using estimation of Spearman's correlation (Dmitriev, 1995). This approach helped to explore the role of transport processes and to reveal the changes which had taken place along the bottom of the landforms. The Spearman's correlation increases in magnitude as X (sample position) and Y (metal concentration or other parameter) become closer to being monotone functions of each other. The sign of the Spearman's correlation indicates the direction of association. The positive sign implies an increase and the negative sign a decrease in the parameter along the sequence.

3. Results and discussion

3.1. Metals contents in the sand fraction of the studied objects

Table 1 summarizes the descriptive statistics of metals contents for the total population of the soil sand samples (n = 49).

Because the data are very heterogenic and are derived from the analysis of very different soil materials the metal contents in the sand fraction of the study area show very high variations. At the same time, the ranges of datasets for all metals, except Mn, appear to conform to the natural geogenic concentrations for sandy parent material of the Russian Plain and Western Siberia as reported by Bogatiryev et al. (2003) and Il'in and Syso (2001). They also support data reported by Baidina (2001) for the sand fraction of humus horizons in some forest soils. The opposite was found for Mn, which concentrations in the studied objects are 2–3 times higher than the typical ranges recorded in the listed literature sources.

The variation coefficients according to Table 1 are diminishing in the order Mn > Fe, Ti, Cr, Cu, Co > Zn, Ni > Zr, Pb. The high variability registered for Mn in the sand fraction was observed also in the other particle size fractions (Samonova et al., 2013). This can be explained by the participation of Mn in oxidation – reduction processes leading to the repeated release of Mn and its precipitation (Kabata-Pendias and Pendias, 2001; Millaleo et al., 2010) in the form of coatings (Eren et al., 2014), nodules and concretions (Gerasimova and Isachenkova, 2003; Vodyanitskii et al., 2003). The high variability recorded for Fe is also related to pedogenic processes involving changes in pH-Eh conditions (Kabata-Pendias and Pendias, 2001; Vodyanitskii et al., 2003) but can also be due to variations in mineralogical composition of parent materials across the study area. The spectrum of heavy minerals and the relative proportion of their fraction in different

Table 1
Descriptive statistics of metals concentrations in soil coarse and medium sand fraction (*n* = 49).

	Minimum	Maximum	Mean	Median	SD	CV%
Fe (%)	0.4	30	6.3	5	5.7	91
Mn (ppm)	150	18,000	2420	1000	3174	131
Ti (ppm)	120	6000	1520	1000	1339	88
Zr (ppm)	30	330	140	130	75.3	54
Zn (ppm)	20	290	64	40	49.0	77
Cu (ppm)	16	400	83	67	69.6	84
Pb (ppm)	8	50	19	17	10.0	50
Co (ppm)	4	76	21	14	17.1	80
Cr (ppm)	17	290	53	41	45.9	86
Ni (ppm)	11	130	39	33	24.6	63

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[1] The results of the study on geochemistry of the erosional systems based on the bulk soil analysis were reported by the authors in Samonova et al. (2014)

Table 2
Selected properties and concentrations of the metals in the fraction 1–0.25 mm.

Horizon	Depth (cm)	pH	Humus (%)	Granulometric fractions, mm (%)						Fe (%)	Pb ppm	Cr ppm	Co ppm	Ni ppm	Mn ppm	Cu ppm	Zn ppm	Ti ppm	Zr ppm
				1–0.25	0.25–0.05	0.05–0.01	0.01–0.005	0.005–0.001	< 0.001										
Sod- weakly podzolic soil with buried horizons, p. 7																			
A	5–11	4.5	2.05	7.7	12.9	48.8	7.9	12.1	10.7	7.1	13	20	20	88	1100	140	30	1300	–
AE	11–29	4.8	1.07	7.8	11.7	42.2	10.3	13.4	14.5	4.5	17	44	21	60	1200	110	30	570	–
BC	29–51	5.2	0.36	23.4	42.5	13.9	1.7	2.8	15.8	2.4	8	30	9	31	380	33	30	470	–
Egb	51–86	5.1	0.21	17.0	44.7	13.6	1.6	5.2	17.8	3.0	8	25	7	29	360	38	30	300	–
Cgb	86–98	5.2	–	9.4	52.3	12.3	2.7	3.8	19.5	5.4	9	80	14	76	620	76	30	400	–
D	98–125	5.4	–	23.2	55.9	2.8	1.1	1.8	15.8	2.4	9	36	7	32	330	26	30	500	–
Soddy soil (*Regosol*), *p. 8*																			
A	8–15	4.8	2.85	3.5	4.7	57.7	13.9	9.9	10.3	5.2	11	38	11	35	2000	66	70	1500	150
AC	45–50	5.5	1.14	2.5	3.0	56.5	12.7	10.4	14.9	13.9	14	150	31	14	1900	210	40	120	–
C	50–105	5.5	–	15.4	36.9	20.1	6.0	8.8	12.7	2.4	12	43	8	38	480	46	30	420	–
Soddy gleic soil (*Gleic Regosol*), *p. 10*																			
A	8–22	4.8	0.72	8.2	10.0	46.4	8.8	10.7	15.9	3.7	11	60	11	54	540	100	30	400	–
ACg	24–79	5.1	1.10	2.6	8.6	54.9	10.5	10.3	13.1	1.4	15	20	9	11	2000	18	30	1900	180
Soddy soil with buried horizons of fluvial soil (*Regosol over Calcaric Fluvisol*), *p. 11*																			
A	0–10	5.9	3.29	9.6	12.0	42.0	9.3	12.3	14.8	10	9	110	13	42	1000	160	40	4500	50
A	10–21	6.5	1.78	6.8	8.4	46.1	12.2	12.3	14.0	30	21	290	49	97	2700	400	290	980	110
C	21–39	6.8	1.65	5.3	3.9	47.2	14.5	13.6	15.4	25	11	66	7	39	1000	170	30	480	30
Akb	39–70	7.5	0.76	25.2	26.7	23.5	4.3	7.3	12.9	5	13	35	8	24	320	59	20	540	30
Ckb	70–89	7.7	–	74.6	15.3	3.0	1.2	0.9	5.0	3	14	18	4	13	150	20	20	540	50
Ckgb	89–110..	7.8	0.43	22.7	24.9	26.7	5.5	5.2	14.9	5	14	80	8	36	320	68	100	470	90
Fluvial calcareous soil (*Calcaric Fluvisol*), *p. 12*																			
Ak	0–14	8.0	5.0	2.3	21.2	54.8	6.9	7.3	7.5	5	24	51	17	33	760	67	110	3300	230
Ak	14–25	8.1	3.09	1.9	21.7	53.3	6.1	9.1	7.8	5	23	49	14	33	700	57	130	4900	330
ACk	25–66	8.6	1.55	2.3	13.0	54.5	10.8	10.3	8.9	15	9	68	18	54	1900	72	60	650	130
ACkb	66–94	8.9	2.28	4.0	12.6	49.8	7.6	12.6	13.3	4	16	28	9	17	540	29	40	1400	130

"–" was not analyzed.

parent rocks defines the initial levels of metal differentiation in sand material across the study area. As it was reported in Rychagov and Antonov (1992) the spectrum of heavy minerals of two till layers (and correspondent glaciofluvial deposits) differs in terms of the abundances of minerals derived from rocks of different provenances. The Dnieper till is rich in the minerals glauconite as well as sulfides derived from local rocks (limestones and dolomites), however in the deposits of the Moscow age these minerals are rare. The Moscow till is characterized by higher abundances of hornblende, garnet and ilmenite, typically found in rocks of Baltic provenance – granites and gneisses. A similar mineralogical spectrum is observed in the heavy fraction of overlaying mantle loam (Rychagov and Antonov, 1992): heavy minerals in its finer sand fraction (0.1–0.25 mm) include hornblende (20 to 40%), garnet (20–30%), ilmenite (10–20%), newly formed iron oxides and hydroxides (7 to 35%) and minor amount of pyroxenes and some other minerals such as epidote, rutile and zircon. Glaciofluvial sands, which often underlain mantle loam are always poorer in heavy fraction but exhibit higher content of newly formed iron oxides and hydroxides.

3.2. Vertical distribution of the metals in the representative soil profiles

The representative soils described here (Table 2) belong to sod-podzolic soils, soddy soils (some with gleyic or calcareous features) and fluvial soils (Table 2). The results of particle-size analyses of bulk samples showed that the amount of the sand fraction in the soils varies within wide limits (from 1.9 to 75%) depending on lithological features of the parent material and underlying strata. Even distribution of the fraction across the soil profiles was not registered. In the soils on loamy deposits the enrichment with sand particles was observed in upper horizons, due to losses of finer material being translocated with infiltrating water while in the soils underlain by sandy glaciofluvial deposits the enrichment takes place in lower soil horizons.

The *soddy weakly podzolic soil with buried horizons* (p. 7, Table 2) which was formed in non-uniform parent materials on the gentle slope segment shows a two-stage profile. The uppermost part of the solum comprises the horizons of a recent soil developed in loess-like deposits composed mainly of silt, while the lower part consists of buried horizons of sandy (sandy loam and loamy sand) texture derived from glaciofluvial strata. The vertical distribution of metals in the sand fraction is irregular and shows different patterns in the upper and the lower parts of the solum. In the upper (loessic) soil horizons the coarse fraction is not abundant but relatively metal-rich: the amount of Fe + Ti + Mn, the elements typical for ferrous compounds, is 2–3 times higher than in the coarse-grained D horizon and buried eluvial horizon Egb showing high sand content (79% and 62% respectively). At the same time, the metal enrichment of the coarse fraction in loessic horizons is not uniform. The maximum levels of Fe, Ti, Ni and Cu are limited to the upper A-horizon, while Mn, Cr and Pb show higher concentrations in the coarse fraction of the AE horizon. In the deeper and sandier horizons the distribution of metals in the coarse fraction is also irregular: relative to the D horizon and buried eluvial horizon the Cg horizon displays twice higher level of Fe + Mn + Ti. The metal enrichment of the coarser fraction in this horizon we relate to changing redox conditions, resulting in neoformation of coarse particles represented by pedogenic iron and manganese nodules and concretions. The co-precipitation of Cu, Cr, Ni, and Co with iron and manganese compounds (Vodyanitskii et al., 2003) explains their high concentrations in this horizon. In contrast to other elements, Zn is distributed evenly throughout both parts of the soil profile.

Thus, the observed results imply that metal contents in the soil sand fraction change along the profile. These changes might be related not only to the genesis of the parent material (loessial or glaciofluvial) but also to soil forming processes which operate in genetically different parts of the solum.

The *soddy soil* (p. 8, Table 2) with weakly differentiated A-AC-C profile was formed on the steep segment of the slope. The parent material is represented by sandy loam diluvium underlain by sandy material. The maximum metal contents are found in the upper A and AC horizons rich in humus, both having a silt or silt loam texture and containing a very low amount of the studied fraction (3.5 and 2.5% respectively). Mn, Zn, Ti show the highest concentrations in the sand fraction of the surface A-horizon (with a transfer factor varying between 2 and 4) while the maximum levels of Fe, Cr, Co, Cu were observed in the AC horizon (with a transfer factor varying between 3 and 5). Pb and Ni exhibited a rather poor differentiation between the surface A-horizon and the parent material.

In *soddy gleyic soil* (p. 10, Table 2), developed in silt loam strata in the bottom of the local depression, gleyic properties were observed not only in ACg horizon but also in the A-horizon. Analyses showed that higher contents of Fe, Cr, Ni, Cu, Co occurred in the sand fraction of the A-horizon, while Mn, Ti and Pb showed to have enriched the sand particles in ACg horizon, Pb and Co do not reveal any significant differences in concentrations between these two horizons, and Zn is characterized by a uniform distribution.

Soddy soil with buried horizons of fluvial soil (p. 11, Table 2) was formed in a gully's fan deposits overlying the floodplain of the Protva river. The soil profile includes two parts − a recent as well as a buried fluvial soil each having specific texture and pH (Table 2). In the sand fraction partitioned from the recent soil, characterized by slightly acidic to neutral reaction and silt to silt loamy texture, the maximum metal concentrations are found in the uppermost A-horizon. In the buried soil with neutral to slightly alkaline reaction and sandy loam texture, higher concentrations of some elements such as Zn, Cu, Ni, Cr, Zr are recorded in parent material Ckgb, while elements such as Fe, Mn, Co show no difference in concentrations between the humus horizon of the buried soil and its parent alluvial material Ckgb. A relatively even distribution is also found for Ti and Pb in the sand fraction of the buried soil.

Fluvial calcareous soil with a buried humus horizon (p. 12, Table 2) was studied in the Protva river floodplain. This soil exhibits consistent silt loam texture and alkaline reaction throughout its profile and at depth is underlain by travertine. In the second humus horizon Ak the studied fraction contains the highest concentrations of Zn, Ti and Zr, while the sand in the following ACk horizon (Table 2) is enriched with other elements. The buried Akb horizon has the lowest levels of Mn, Co, Cr, Ni, Cu, Zn. This change across soil horizons is not related to humus content but more likely influenced by the genesis of the sand fraction in the fluvial sediments, which can be derived from different sources.

Thus, the analysis of the vertical distributions of the metals in the sand fraction partitioned from different soils revealed that metals accumulate either in humus horizons or in the underlying strata, but the elements with similar distribution might be present in different element associations. The genesis of the sand fraction defines the initial concentrations of the metals, however the subsequent transformation of this fraction which takes place in homogeneous parent material is more likely to be conditioned by pedogenic and geochemical processes such as mineral weathering and breakdown, reduction and oxidation with neoformation of Fe and Mn hydroxides, the formation of organic complexes and fixation of the elements in horizons rich in humus.

3.3. Spatial patterns in metals distributions in the sand fraction of the studied objects

Downslope migration of various substances in soil catenas and small erosional landforms occur in a chemical form and/or in associations with soil particles. Downslope migration is an important factor which defines the redistribution of metals at landscape level. Physical migration of the soil particles can be a result of erosional processes, such as slope wash or solifluction, which occur during heavy rainstorms in summer and during snowmelt in spring. The snowmelt period is considered to be one of the most important contributors to sediment production in the study area. Slope wash and solifluction processes prevail especially on cultivated watershed slopes, causing average rates of soils loss varying between 0.14 and 5.2 t ha^{-1}, depending on slope features and type of agrocoenosis (Golosov, 1996). Hillslopes covered with grassy vegetation mobilize ten to hundreds times less sediment (0.013 t ha^{-1}). The results of the erosion measurements performed during snowmelt period showed that the products of snowmelt are transported ten times more effectively than the products of rainfall erosion: 24% of this reach rivers, while substantial volume of the rainfall-induced erosion products (98%) are redeposited in within-slope sinks and do not even reach the slope toes and gully heads (Golosov, 1996).

Fig. 4 displays the average, minimum and maximum concentrations of metals in the sand fraction across the two catenary systems and two erosional landforms studied.

Descriptive statistical analysis performed for the subpopulation of topsoil samples ($n = 35$) (in respect to total population analysis, $n = 49$) showed a clear decrease in variation coefficients for Mn (from 131 to 92%) and Co (from 80 to 69%) as well as a weaker drop in variation for other elements, except Fe, Zn, Cr and Cu. The values of variation coefficients estimated for Fe and Zn do not imply any changes, while for Cr and Cu they display a shift to a little higher variation. The elements can be ranked by decreasing Cv values as follows: Cr, Mn, Fe, Cu (94–89%) > Ti (82%) > Zn (76%) > Co, Ni (69%) > Zr, Pb (47–45%).

3.3.1. Catenas

Catena 1 has the length of 200 m. It faces the river valley and is located on the right bank of the Protva river (Fig. 1). The uppermost positions are characterized by sod-podzolic soils on mantle loam, which down the slope are replaced by soddy soils on diluvium (Fig. 2). At footslope positions soddy soils show calcaric features due to the presence of calcareous rock fragments in the subsoil (Fig. 2). The studied soils differ in terms of general properties responsible for metal mobilization. The soils in upper sections of the catena 1 are acidic and slightly acidic (pH 5.1 − 6.4) and those of lower sections are neutral (pH 7.2 − 7.4). Humus content increases along the catena from 1.7 to 3.2%.

The length of *catena* 2, that ends in a gully's bottom and crosses its north-western slope (Fig. 1), is about 180 m. Its soil cover is characterized by sod-podzolic and soddy soil types (Fig. 2). The three of five soil profiles of *catena* 2 are described in the above section concerning the vertical distribution of the metals. In contrast to *catena* 1, the soils of *catena* 2 are entirely acidic (pH 4.8 − 5.0) and distinguished by an opposite patterns in humus distribution going from top to bottom: the topsoil of upper sections of *catena* 2 contains about 2–3% of humus and the soil in the gully's bottom only 0.7% (Table 2). These lowermost elements in the catenary sequence receive run-off water and are represented by wetter varieties of soddy soils, showing features of gleyzation.

Although the forested catenas are considered to be rather stable in terms of slope wash and solifluction activity, the rate of these processes might have been higher in the past. In some positions, especially in the lower slope sections with higher slope gradient, sheet erosion and solifluction usually show a higher intensity. Soils in such positions are also subjected to active displacement due to creep, considered to be one of the most common processes in the areas with natural vegetation. An experimental study of soil movement along the Protva river valley side and along gully slopes in relation to the soil depth reported in (Golosov, 1996) revealed that the maximum displacement (1.5 to 6 mm year^{-1}) occurs in the upper 40–60 cm of soil bodies while in the deeper strata the movement is limited to 0.1–0.3 mm year^{-1}. The study also showed that creep processes intensify with increasing slope gradient, and that the rate of soil displacement along the gully side is higher compared to the valley sides, attributed to the fast removal of sediments by temporal streams in the gully's bottom (Rychagov and Antonov, 1996).

The results of granulometric analysis imply some spatial patterns in distributions of size fractions. The highest amounts of sand in the topsoil of the both catenas are observed in the downslope segments (Fig. 5), with the proportion of the 1–0.25 mm fraction increasing from

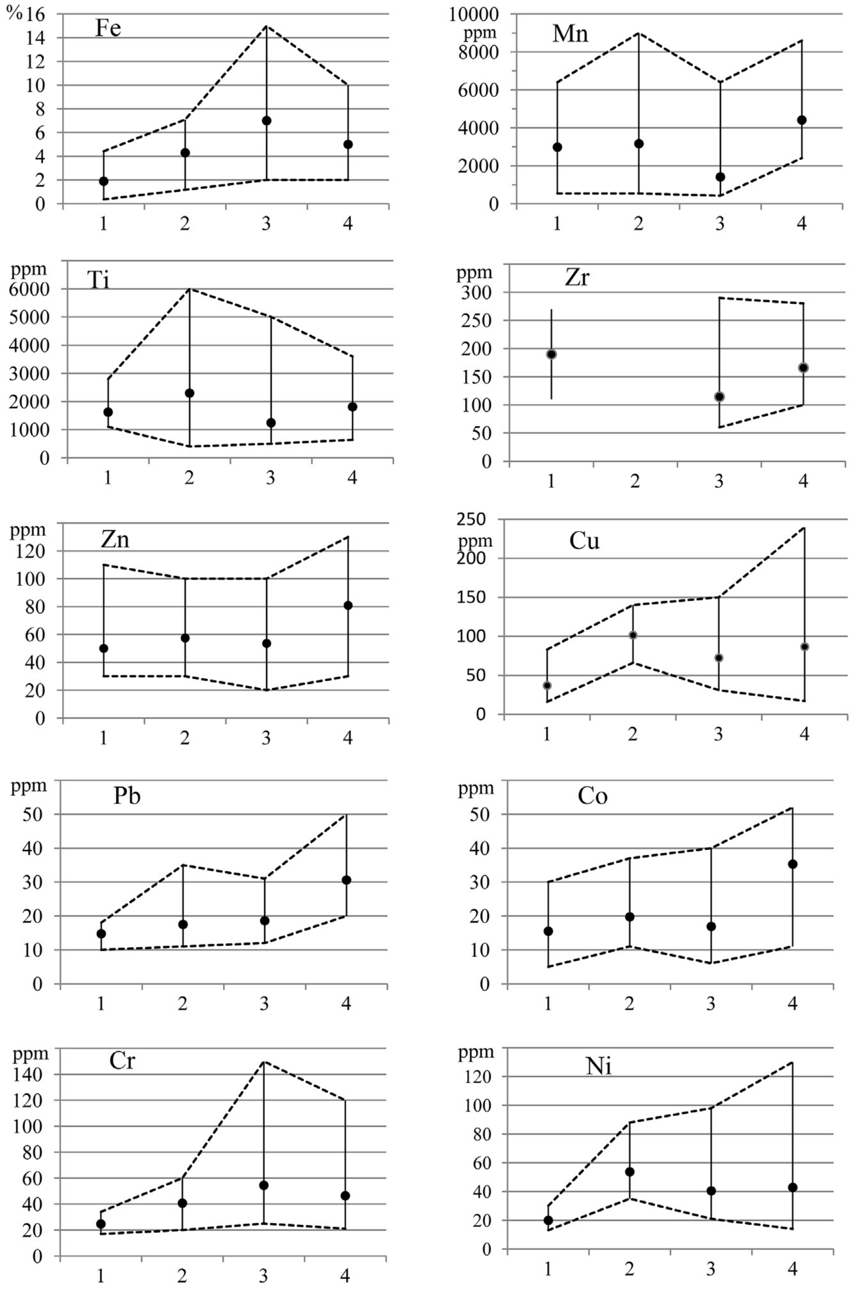

Fig. 4. Graphical representation of metal contents (arithmetic mean, minimum and maximum concentrations) in the fraction 1–0.25 mm across the studied systems (topsoil horizons): 1 – *catena 1*; 2 – *catena 2*; 3 – the gully (with its adjacent areas); 4– the *balka* (with its adjacent areas).

0.8–2% to 7–8%. This trend corresponds to differential textural features of parent materials and underlying strata, represented in the lower parts of the slopes by sandy moraine (*catena* 1) and glaciofluvial deposits (*catena* 2).

The estimated median concentration of the 1–0.25 mm fraction partitioned from the topsoil of the two catenas ($n = 8$) equals 2.7% for Fe; 1550 ppm for Mn; 1350 ppm for Ti; 180 ppm for Zr; 74 ppm for Cu; 50 ppm for Zn; 32 ppm for Cr; 32.5 ppm for Ni; 14.5 ppm for Co; and 13 ppm for Pb.

Catena 1 is characterized by relatively low metal contents in the sand fraction. The following concentrations of the elements were determined in the summit positions: 1.6% for Fe; 6400 ppm for Mn; 1400 ppm for Ti; 110 ppm for Zn; 27 ppm for Cu; 18 ppm for Cu; 18 ppm for Pb; 17 ppm for Cr; 13 ppm for Ni. Along the slope the geochemistry of the soil sand fraction is not constant: the largest variations were exhibited by Mn, Cu, Zn, Co and Fe. For the majority of the elements (Fe, Co, Pb, Cu, Zr, Ti) the minimal concentrations were found in soils developing on the steep sections of the slope (Fig. 5). Compared with the reference (summit) soil, the topsoil of the gentle slope section showed 1.5–2 times higher concentrations of Cr, Co, Ni, Ti and Zr. In the lowermost positions of *catena* 1 the concentrations of Cu, Fe, Ni and Cr reach their maximum levels, and their estimated L coefficients equal 3.1, 2.7, 2.3 and 2.0, respectively. The relative increase in the amount of Fe and the associated metals in the sand fraction registered in the topsoil of this catenary position underlain by calcareous till of the Dnieper age (which the heavy mineral spectrum differs from other Quaternary sediments) might be associated with two factors: the variations in mineralogical composition of the soil particles and the pH increase, promoting the precipitation of Fe compounds and associated metals. In contrast to the metals enriching the soils of the lower slope position, Mn, Zn, Co and Pb exhibited depletions patterns: for Mn the coefficient L equals 0.1, for Zn – 0.3, for Co and Pb – 0.5 and 0.7, respectively (Fig. 5).

The reference (summit) soil in *catena 2* is characterized by relatively high concentrations of the elements in the sand fraction of the topsoil, being 1.2% for Fe; 9000 ppm for Mn; 6000 ppm for Ti; 100 ppm for Cu;

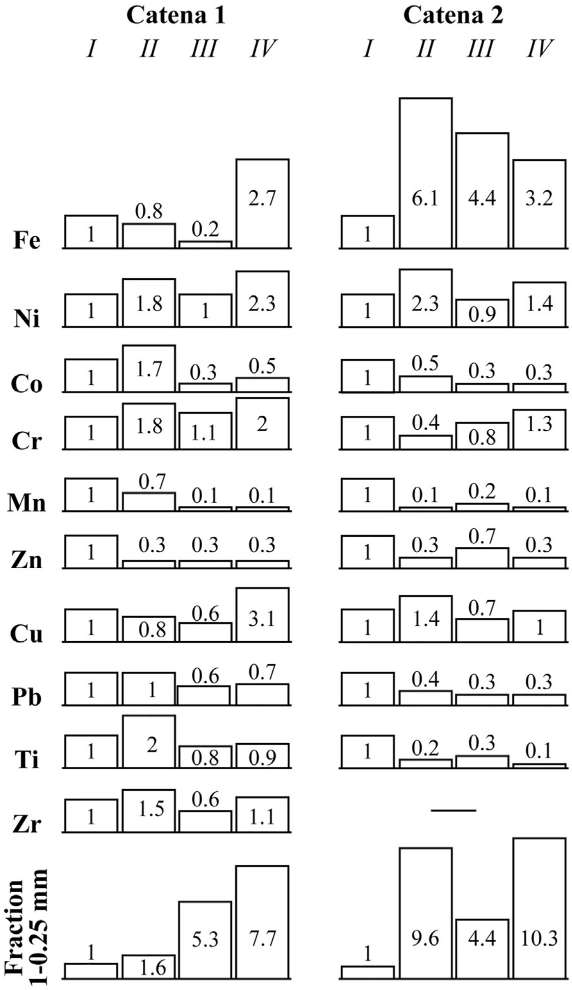

Fig. 5. Values of L coefficients for metal concentrations and the content of the sand fraction along topsoils of two catenas. *I–IV* – positions along the catenas; *I* – summit position, *II* – slope position (gentle section of the slope, angle 2–4°); *III* – steep slope position (angle > 10°); *IV* – footslope and toeslope positions.

100 ppm for Zn; 45 ppm for Cr; 37 ppm for Ni and Co; 35 ppm for Pb. Compared to the reference soil of *catena* 1, the enrichment of the sand fraction with metals is nearly 4 times for Ti, Cu, 3–2 times for Ni, Cr, Co, Pb and 1.4 times for Mn. Since the reference soils in the both catenas are developing on the similar parent material, the most likely explanation of the differences in metal concentrations is the spatial variation in the mineralogical compositions of the sand fraction in mantle loam reported in Rychagov and Antonov (1992).

As concerns the lowermost positions of *catena* 2, the sand fraction is enriched with Fe (L = 3.2), Ni, Cr (L = 1.4–1.3) and depleted in Mn, Ti (L = 0.1), Zn, Pb, Co (L = 0.3), (Fig. 5), indicating that except for Fe the enrichment of the fraction is lower than the depletion. The most unevenly distributed elements are Mn, Ti, Zn, Fe, Pb and Co: the differences in their concentrations along the *catena* can reach 3–10 times. The maximum concentrations occur either in the soils of the summit positions (Mn, Ti, Zn, Pb, Co) or in the soils of the gentle section of the slope (Fe, Ni, Cu) (Fig. 5).

The analysis of 1–0.25 mm fraction geochemistry along the topsoil of the two catenas revealed common patterns in the lateral metal distributions: in both soil sequences we found a decrease in Mn, Zn, Pb, Co, Ti and an increase in Fe, Cr and Ni concentrations in the lower sections of the slopes. Also the data show that for both catenas the topsoils of these lower slope positions are more similar in terms of metal concentrations than the reference soils of the summits (Fig. 6). This implies that soil and geochemical processes along hillslopes, together with the mixing effect of erosional processes such as solifluction and creep, causes geochemical convergence (increase in similarity) of the sand fraction, although different metals might participate differently in these processes. Among the metals, Pb, Co, Cu turned to be most conspicuous. Comparable convergence of physico-chemical properties and bulk metal concentrations in topsoils in the study area in different soil parent material was also reported earlier by Samonova (2002).

3.3.2. Gully and balka systems

Table 3 presents the data on metals concentrations in the fraction 1–0.25 mm, separated from the subsets of topsoil samples collected in different geomorphic units of the erosional landforms.

Gully

In various geomorphic units of the gully system the 1–0.25 mm fraction is distributed very unevenly. The proportion of the sand fraction increases from the adjacent area towards the slope unit, bottom and fan from 4.2% to up to 31.8%, which can be explained mostly by the heterolithic nature of the system related to the gully's incision into glaciofluvial strata. The fact that the topsoil of the fan contains more sand (and less fine) materials than the bottom unit is likely due to redistribution of sediments in longitudinal direction, taking place during summer rainstorms or spring snowmelt. The signs and the magnitudes of the Spearmen's coefficients, estimated for the gully's longitudinal sequence (n = 11), confirm that along the bottom in downward direction the content of coarse and medium sand consistently increases (Samonova et al., 2014).

The metal concentrations in the sand fraction vary within wide limits and for most elements the variation coefficients exceed 50%. Specifically Ti and Mn show Cv values of 101 and 128%, respectively, while the lowest Cv value was found for Pb (Cv = 30%).

The highest element concentrations, except of Ti, in the sand fraction are observed in soils of the gully's adjacent area (Table 3), where soil parent material is represented by mantle loam. The L coefficients, estimated for the slope and bottom units, have values < 1, indicating that sand particles in the internal parts of the catenary system are depleted in metals compared to the adjacent reference unit. This reduction in metal concentrations is mainly caused by the incision of the landform into glaciofluvial deposits which are poorer in heavy minerals than loessial loam. Taking into account the intensity of depletion in the slope unit, the metals are ranked in following order: Mn (L = 0.2) > Zn, Cu, Co (0.3) > Ni (0.4) > Cr (0.5) > Fe, Zr (0.6) > Pb (0.7) > Ti (0.9). Compared to the slope unit, the concentrations in the gully bottom of Zn, Ni, Cr are observed to be 1.5–2 times higher, while the concentrations of other metals did not change (Co) or showed only a slight difference (for Mn, Ti, Fe, Zr).

The minimal concentrations of Pb, Co, Cr, Mn, Zr, Fe occur in the sand fraction of the fan unit (Table 3). Since this unit also showed an accumulation of Ti, these low contents hint at the enrichment of the sand fraction with quartz and Ti-bearing accessory minerals and a depletion in unstable minerals due to transport and weathering processes (Shvanov, 1987). The mineralogical data for the fine sand reported in Panin et al. (2011) support these findings, as the upper unit of the gully's detrital fan is characterized by a relatively high content of ilmenite and a low content of hornblende. The signs and the magnitudes of the Spearmen's coefficients ($r = -1$ and $r = -0.9$, $p < 0.05$), estimated for the gully's longitudinal sequence ($n = 5$), confirm that in downward direction (along the bottom of the gully) the contents of Mn, Pb and Co consistently decrease. Comparable, but less significant, tendencies are found for Fe, Zr and Cr ($r = -0.8$ for Fe and $r = -0.7$ for Zr and Cr).

Balka

Compared to the gully, the distribution of grain-size fractions across various geomorphologic units of the *balka* is more invariant, except of the sand fraction, for which the content in the topsoil of the slope unit (11%) is higher than in the adjacent area (6%) or in the *balka*'s bottom (4.3%). Since according to Panin et al. (2009) the sandy stratum on the

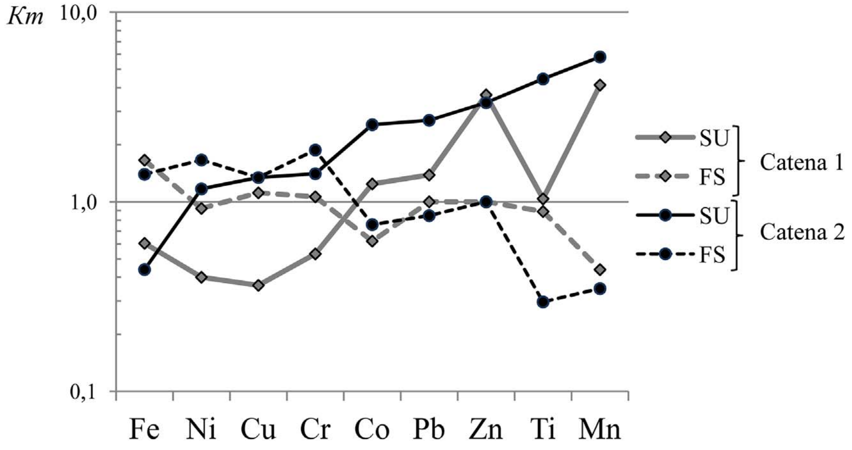

Fig. 6. Standardized values of metal contents in the sand fraction, normalized to median concentrations, in topsoils of catenary sequences: Su – summit position; FS – footslope and toeslope position.

landform slopes occurs at depths of > 1 m, it probably has little influence on the topsoil granulometry. Instead the increase of the sand fraction in the surface horizon might be associated with the fluxes of soil material from cultivated source areas (Golosov, 2006a, b). When analyzing the *balka*'s longitudinal variations in granulometry ($n = 16$), we found linear trends similar to those in the gully: the amount of sand fractions increases consistently towards the lowermost positions ($r = 0.72$ for the coarse sand fraction) while the amounts of finer fractions (silt and clay) decrease ($r = -0.54$).

Variation coefficients of most metals are in the range of 30–60%. For Ni and Cu they reach 77 and 78%, respectively, for Pb the variation coefficient equals 32%. Compared to the adjacent areas the sand fraction of the slope unit shows somewhat higher concentrations of Mn and Co (L = 1.4–1.3), nearly equal concentrations of Zn (L = 1.1) and Pb (L = 1), and lower concentrations of the majority of the elements Cu (L = 0.4), Fe, Cr, Ni, Ti, Zr (L = 0.6–0.7). In the bottom unit the sand fraction tends to accumulate some metals such as Cu, Ni, Cr, Zn (L = 1.3–1.6), while other elements are found in lower (Mn, Pb) or nearly equal concentrations (Co, Ti, Fe, Zr). The fan is characterized by maximum concentrations of Ti, Zr, Pb (Table 3) and minimal levels of Cu and Fe, while the contents of Ni, Cr, Co, Zn are nearly the same as in the slope unit (Table 3).

Comparing the two landforms shows that there are some common patterns in the sand distribution across various units: in respect to the adjacent areas the slope units are enriched with the sand fraction. Also in longitudinal soil sequences in downward direction the amount of the sand consistently increases. However, there are also some distinct differences between the systems with respect to the sand distribution across the slope and bottom units: in the gully the bottom unit tends to accumulate the sand due to its deep incision into glaciofluvial strata, while in the *balka* the higher proportion of sand is limited to the slope unit and is likely related to the fluxes from upward positions.

With respect to the distribution of metals in the sand fraction, the study shows that in the *balka* system the changes across its elementary units are less remarkable than in the gully. This fact can be explained by more homogeneous lithological features and similar genesis of parent materials in the *balka*, compared to different genetic sources of sands in the gully. At the same time, in addition to the differences, there are also common patterns in element distributions: compared to the adjacent areas for the both systems the study shows a depletion of Fe, Cu, Ni, Cr, Zr in the slope units and the enrichment in the bottom units with Zn, Cu, Ni and Cr (relative to the slopes). Other metals behave differently in the *balka* and the gully systems. These findings reveal that metal contents and distributions in the sand fraction are indicative both of their genetic source as well as lateral migration processes, responsible for the transformation the sand related to the dynamics of metal losses and enrichments across various landforms units. Identification of groups of elements with common distribution patterns supports the idea that chemical transformation of the fraction during the lateral transport through the studied systems is mainly related to the dynamics of iron and associated elements.

The correlation analysis performed for the subpopulation of the sand samples from the surface soil horizons ($n = 35$) showed that Fe was positively correlated with Cr, Ni, Cu, Zn ($p < 0.001$) and Co ($p = 0.04$). All listed elements also have very close relationship with each other ($p < 0.001$). They can be found in primary and newly

Table 3
The distribution of the metals concentrations in the fraction 1–0.25 mm partitioned from the humus horizons across the gully's and balka's units.

Elements	Gully				Balka			
	Adjacent area ($n = 4$)	Slope unit ($n = 3$)	Bottom Unit ($n = 3$)	Fan Unit ($n = 1$)	Adjacent area ($n = 4$)	Slope unit ($n = 4$)	Bottom Unit ($n = 3$)	Fan Unit ($n = 1$)
Cu (ppm)	**115.3**[a]	37.7	57.0	51	95	42	**128**	29
Zn (ppm)	**80.0**	20.0	63.3	20.0	66.7	76.7	**95.0**	80.0
Pb (ppm)	**22.3**	16.0	18.7	12.0	32.3	32.3	25.0	**42**
Co (ppm)	**30.0**	10.0	10.0	6.0	28.7	37.7	**39.0**	34.0
Ni (ppm)	**62.8**	23.3	34.0	22.0	40.0	22.3	**65.0**	25.0
Cr (ppm)	**77.5**	35.0	53.3	25.0	45.0	28.7	**65.0**	33.0
Mn (ppm)	**2810**	607	670	450	3867	**5567**	3850	4800
Ti (ppm)	900	810	893	**5000**	2100	1346	1500	**3600**
Zr (ppm)	**160.0**	93.3	86.7	80.0	170.0	113.3	183.3	**260.0**
Fe (%)	**10.3**	6.0	5.3	2.0	**6.3**	3.7	5.7	3.0

[a] Bold font is given to the maximum concentrations of an element for each system.

formed Fe-bearing minerals, which are reported to be active sorbents for many metals (Acosta et al., 2011; Kabata-Pendias and Pendias, 2001). Specifically Mn was correlated with Co and Pb, while statistically significant correlations ($p = 0.04$) were found also between the following pairs of metals: Mn-Zn; Mn-Zr; Ti-Zr; Pb-Zn. The correlations between metal concentrations in the sand fraction may indicate their presence in some minerals, although a number of authors relate the correlation among elements to their common behavior in soils and in the environment (Acosta et al., 2011). The possible explanation of the correlation between Mn and Zn is the involvement of these elements into biogenic processes, both being essential elements associated with many organic compounds (Kabata-Pendias and Pendias, 2001), and Co in soils always being incorporated in Mn oxide fraction (Zyrin and Titova, 1979). The association between Cr-Ni-Cu-Zn, Pb-Mn-Co, Mn-Zn in bulk soils of the study area was reported earlier in Samonova et al. (1998) and Samonova et al. (2013).

4. Conclusions

The ranges of metal concentrations in the soil sand fraction 1–0.25 mm, except of Mn, appear to conform to the natural geogenic concentrations for sandy parent material of the Russian Plain. The concentrations of Mn are 2–3 times higher than previously reported in literature. Most metals − Fe, Ti, Cr, Zn, Cu, Co–exhibit high natural variability of their concentrations (Cv = 80–90%). The highest variation (> 100%) is found for Mn, the lower variations (60–50%) are displayed by Zr, Ni and Pb.

The vertical distributions of the metals in the soil sand fraction of the study area are not uniform: in most cases the enrichment occurs in the topsoil, where humus accumulation, biogeochemical processes and sand grain weathering take place more actively. In some cases the metals tend to accumulate in parent material or underlying strata. The associations of the metals with similar features of the vertical distribution vary depending on the textural differentiation of the soil profiles.

The analysis of 1–0.25 mm particles' geochemistry in the topsoil of the two forested catenas revealed common patterns in the lateral metal distributions: for both soil sequences we found a decrease in Mn, Zn, Pb, Co, Ti and an increase in Fe, Cr and Ni concentrations in the lower sections of the slopes. The sand fractions in these positions tend to be more similar in terms of metal concentrations than in the reference soils of the catenas' summits. This implies the importance of soil and geochemical processes in the convergence of metal concentrations, which is especially conspicuous for Pb, Co and Cu.

Comparing two small erosional landforms in terms of differentiation of metal contents in the sand fraction across their elementary geomorphic units revealed similar patterns in the lateral distribution of Fe, Cu, Ni, Cr, Zr, Zn and a different behavior of Pb, Co and Mn.

The features of vertical (within the soil profiles) and lateral (along catenas and small erosional systems) distributions of metals are significantly controlled by the genesis of the sand fraction (loessial, glacial, glaciofluvial), although some variations in metal contents are explained to be due to the influence of various pedogenic and geochemical processes, accompanying soil formation and the translocation of sand particles along slopes. The importance of these processes in geochemical transformation of the sand fraction is inferred from the non-uniform distribution of the metals in soils with genetically and lithologically homogeneous parent material and from the similarity in lateral distributions of some element groups along different soil systems.

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