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DISTRIBUTION OF METALS IN PARTICLE SIZE FRACTIONS IN SOILS OF TWO FORESTED CATENAS (SMOLENSK–MOSCOW UPLAND)

ABSTRACT. The concentrations and distribution of Fe, Ti, Zr, Mn, Cu, Ni, Co, Cr, Pb, and Zn associated with various particle size fractions have been analyzed in soils of two forested catenas located in the middle Protva River basin on the Smolensk–Moscow Upland. The results showed that concentration of metals in a particular size fraction was defined by a complex of factors: element chemical properties, soil type, genesis of a soil horizon, and position in the catena. A clearly defined relationship between the fraction size and metal concentrations was found for Ti and Zr. The highest levels of Ti were found in coarse and medium silt, while Zr had its highest values only in coarse silt and, in some cases, in fine sand. Such metals as Fe, Mn, Co, Cu and Pb had high concentrations in sand, fine silt, and clay fractions depending on a soil type and a genetic horizon. The maximum load of Cr, Zn, and Ni (in the majority of cases) was found in clay fraction. The minimum loads of Fe, Mn, Co, Cu, and Ni were found in the coarse silt fraction. Variation in concentrations of heavy metals differed depending on particle size. For most metals, the variations were decreasing from coarser to finer fractions.

KEY WORDS: soils, heavy metals, grain-size fractionation, vertical and lateral distribution patterns.

INTRODUCTION

In ecological assessment of the soil cover, it is important to know background (reference) patterns in distribution of toxic elements, specifically, heavy metals (HMs). Texture is proved to be one of the major factors controlling metal concentrations in soils. A wide range of metals is abundant in finer fractions that are more easily trans-located within soil profile and down the slope [Plyaskina and Ladonin, 2005]. However, some aspects of the particle size distribution and its relationship to metal concentrations have not yet been studied. Little is known, for example, about the distribution of metals across particle size fractions in soils of catenary systems. The purpose of this study is to analyze distribution patterns of metals in the particle size fractions in two soil catenas located in southern taiga zone of the Russian Plain.

STUDY AREA

The study area is located 90 km to the southwest from Moscow on the Smolensk–Moscow Upland (314 m asl). The climate of the study area is humid-temperate-continental with moderately moist, warm summers (mean $T_{July} = 17,5^{\circ}C$), cold winters (mean $T_{January} = -9,9^{\circ}C$), and mean annual precipitation of about 600 mm. The

present-day morphology of the study area is represented by glacial relief on interfluves dated to the Moscow glaciation and the post-Moscow fluvial relief of river valleys and gullies. Boulder clays, silts, and sands of the glacial and glaciofluvial origin serve as parent materials for soil formation; the most common parent material on interfluves is mantle loam that overlays all types of the Quaternary deposits. In the soil cover of the study area, podzoluvisols (sod-podzolic soils, according to the Russian classification) with the medium humus content dominate. Natural vegetation varies because the territory is located in the transition zone from mixed to deciduous forests. Typical are secondary mixed small-leaved and spruce or oak and linden-spruce forests that cover about 60% of the studied area. Arable lands and meadows occupy about 40% of its territory.

MATERIALS AND METHODS

Two heterolithic catenas typical of the study area were selected for the research. Catena 1 ends in a local depression – a gully bottom. Catena 2 faces the river valley. Major positions along the catenas were defined and the soils of these positions were described and sampled. Catena 1 included sod-podzolic soils with AEBtC profile (the watershed summit and slope positions) and soddy soils with AC profile (footslope positions). Catena 2 represented a toposequence of sod-podzolic soils and soddy soils at footslope with calcaric features due to the presence of calcareous rock fragments in subsoil (Fig. 1).

Chemical (pH, organic carbon) and granulometric analysis was carried out on 35 samples taken from genetic horizons of the studied soils. 20 samples were fractionated into 6 (1–0,25 mm, 0,25–0,05mm, 0,05–0,01 mm, 0,01–0,005 mm, 0,005–0,001 mm, < 0,001 mm) or 4 size classes (1–0,25 mm, 0,25–0,05 mm, 0,05–0,01 mm, < 0,001 mm) depending on soil position in the catenas (watershed summit soils – 6 fractions; slope-footslope soils – 4 fractions). All fractionated samples of catena 1 and topsoil samples

of catena 2 were analyzed for Ti, Zr, Mn, Cu, Ni, Co, Cr, Pb, and Zn concentrations using quantitative spectral analysis. Fe was determined using atomic absorption. Statistical treatment included correlation analysis and descriptive statistics, and was performed using SPSS.

Two types of coefficients were estimated to describe the vertical and catenary distribution of the elements and particle size fractions: the first, R – coefficient, is the ratio between the studied parameter in a horizon and the same parameter in the parent material of the soil. This coefficient is used to highlight changes that take place during pedogenesis. The second, L – coefficient, indicates granulometric or geochemical differences between soils of summit positions and subordinate landscapes of the lower parts of a catena. For calculating this coefficient, soils of summit positions are used as reference objects.

RESULTS AND CONCLUSIONS

The studied soils differed in terms of general properties responsible for metal mobilization. The soils in the upper sections of catena 2 are acidic and slightly acidic (pH 5,1–6,4) and those of lower sections are neutral (pH 7,2–7,4). The humus content varied from 2 to 4%. The soils of catena 1 are entirely acidic (pH 4,8–5,0). The soils in the lowest section of the catena receive more water and, therefore, show features of gleyzation. The humus content in the soils of the watershed and slope positions and especially in the gully bottom was lower than in the soils of catena 2 (about 2–3% in the soils of the watershed summit and slope positions and 0,7% in the gully bottom).

The results of physical fractionation analysis have shown that B and C horizons of the studied soils are rich in clay. Where podzolization and lessivage take place, the maximum clay accumulation was observed in Bt horizon. An even distribution across the vertical sequence of the soil horizons was typical of medium silt (0,01–0,005 mm).

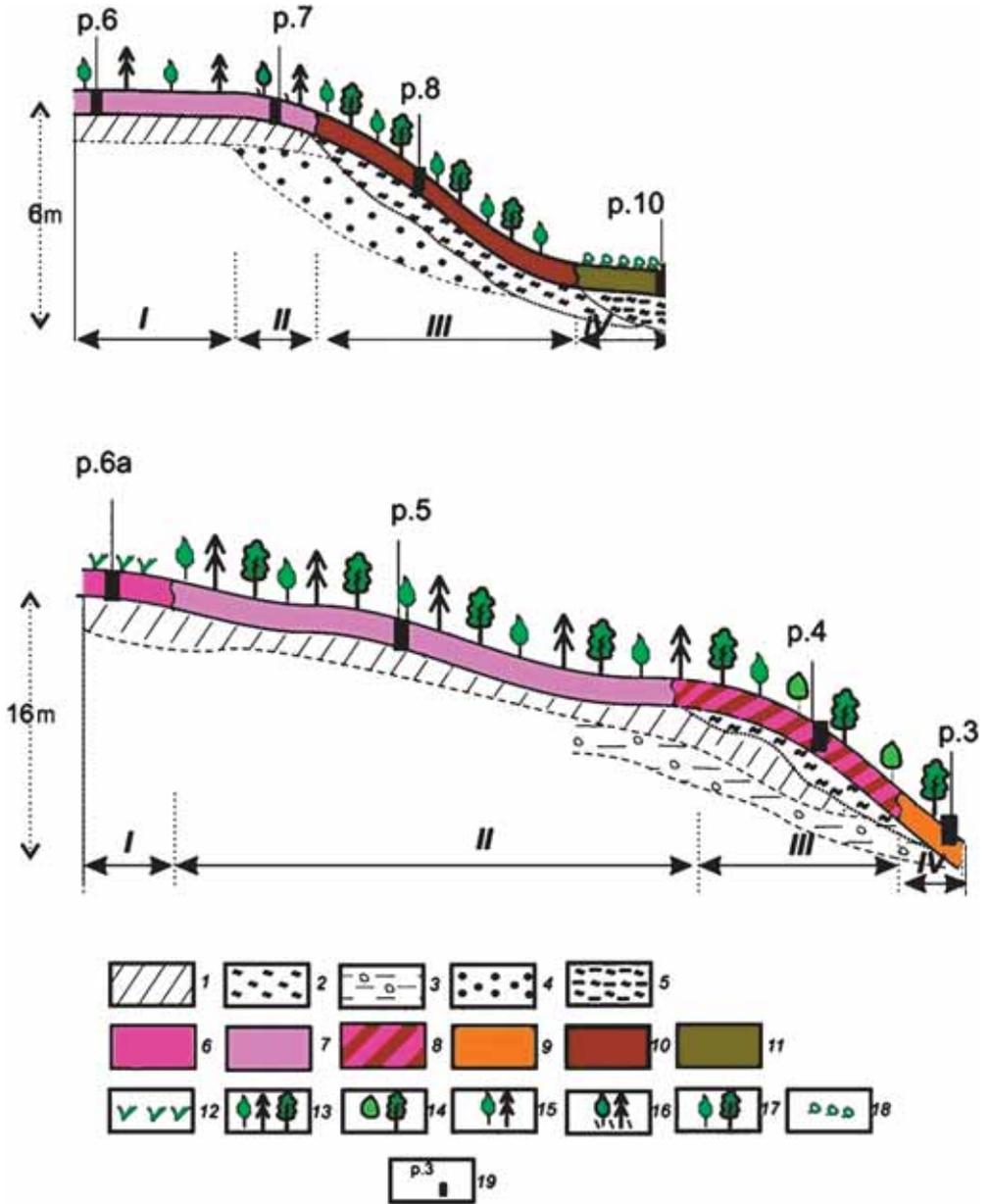


Fig. 1. The studied soil catenas (catena 1 – above, catena 2 – below).

Catenary positions (I–IV): I – watershed summit positions; II–III slope positions;

IV – footslope and toeslope positions;

Quaternary deposits (1–5): 1 – mantle loam, 2 – loamy deluvium; 3 – calcareous glacial loam;

4 – glaciofluvial sands; 5 – loamy deluvium and proluvium;

Soils (6–11): 6 – sod-podzolic soils (podzoluvisols), 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-linden forest; 15 – birch-spruce forest; 16 – aspen-spruce forest; 17 – birch-oak forest;

18 – forest herbaceous community;

19 – names and locations of the soil profiles

In some cases, this size fraction was abundant in topsoil rich in humus. Fine silt accumulates in humic horizons. The vertical distribution of coarse and medium (1–0,25 mm) and fine (0,25–0,05 mm) sand didn't show any clear patterns. The obtained results indicate that the vertical distribution of two particle size fractions – fine silt and clay – was associated with soil forming processes. For fine silt, it was the accumulation of organic material in the surface horizons, and for clay – a combination of the eluvial and illuvial processes.

The results of chemical analysis of the fractionated soil materials are represented in Table 1. It shows the simple average (in the numerator), minimum, and maximum values (in the denominator) of the HMs concentrations in each of the particle size fractions.

The physical size fractionation of the HMs showed that their concentrations depended on the genesis of both the fractions and the horizons. A clearly defined relationship between the fraction size and the highest concentrations was for Ti and Zr. The highest levels of Ti were found in coarse and medium silt (0,05–0,01 mm, 0,01–0,005 mm), while Zr had the highest values only in coarse silt and in some cases in fine sand (0,25–0,05 mm). High load of Ti in silt fractions have been described by I.G. Pobeditseva [1975] who associated it with the abundance of some primary minerals.

Such metals as Fe, Mn, Co, Cu, and Pb can accumulate in sand, fine silt, and clay fractions depending on the soil type, genetic horizon, and position in the catena. The maximum load of Cr, Zn, and Ni (in most

Table 1. Concentrations of HMs (ppm) in particle size fractions in the soils of the catenas

Metals	Particle size fractions, mm					
	Coarse and medium sand	Fine Sand	Coarse Silt	Medium Silt	Fine Silt	Clay
	1–0.25 n = 19*	0.25–0.05 n = 19	0.05–0.01 n = 18	0.01–0.005 n = 7	0.005–0.001 n = 7	<0.001 n = 18
Pb	16.3 8–43	20 9–37	23.8 17–44	27.1 15–43	38.0 28–49	33.6 20–49
Cr	50.3 20–150	49.4 23–84	64.8 54–88	69.3 54–100	97.9 72–120	112.6 96–130
Co	21.9 7–76	14.6 4–27	9.5 6–30	12.9 8–25	22.6 14–31	24.9 20–32
Ni	44.6 14–88	35.8 13–60	20.1 13–51	32.7 20–63	63.7 42–80	80.5 70–88
Mn	3082.7 330–18000	2840 350–15 000	522.1 350–820	451.4 330–600	717.1 420–1100	1459.3 400–5600
Cu	88.1 26–210	59.7 14–120	22.2 12–78	52.6 21–110	109.4 68–190	107.3 82–200
Zn	46.4 30–130	65.3 30–150	70 40–140	145.7 80–220	208.6 150–300	240 160–370
Ti	1198.2 120–6000	3806.7 1900–7000	8271.4 6700–10 000	8800 1200–12 000	7171.4 5600–11 000	6178.6 4200–9000
Zr	85 50–170	706.4 270–1700	1159.2 850–1500	357.5 250–510	203.3 160–250	173.9 130–210
Fe,%	3.9 0.4–13.9	3.2 0.5–6.9	1.8 0.6–5.2	2.1 1.4–2.4	5.0 3.4–8.0	5.6 4.6–7.3

n – number of samples.

**Table 2. Element associations in the fractionated soil material
(based on the correlation analysis of data for catena 1)**

Particle size fraction, mm	Element groups	
	Correlation between elements is significant at 0.01 level	Correlation is significant at 0.05 level
1–0.25	Pb–Mn–Co–Zn	
0.25–0.05	Cr–Cu–Ni–Co; Zn–Cu–Co; Pb–Co–Ti	Ti–Mn
0.05–0.01	Cu–Cr–Pb–Ni–Co; Zn–Co–Ni–Pb–Cu	
0.01–0.005	Cu–Cr–Pb–Ni–Co–Zn	Zn–Co–Ni
0.005–0.001	Ni–Co; Ni–Cr	Cu–Co
<0.001	Mn–Zn; Mn–Co	Pb–Co; Pb–Cu

cases) was found in the clay fraction. This can be explained by element sorption on clay minerals and organic matter [Titova et al, 1996]. Ni had either the maximum or second to maximum concentration in sand fraction (1–0,25 mm) depending on the genetic horizon. The minimum load of Fe, Mn, Co, Cu, and Ni was found in the coarse silt fraction, which can be a result of eolian origin of this fraction and/or epigenetic transformation during pedogenesis. The concentration of metals in a particular size fraction was defined by a complex of factors: element chemical properties, soil type and genesis of a soil horizon, as well as the position in the catena.

Correlation analysis has shown that the Co, Fe, Cr, Ni, and Cu concentrations in the bulk samples were linearly dependent on the clay fraction content, whereas Mn, Zn, and Pb were connected with the amount of the silt fraction. The Cr and Pb concentrations were controlled mainly by the amount of the sand fraction in the soil samples.

Statistical treatment of the particle size fraction subpopulations allowed us to identify the interrelated element groups typical of specific size fractions. They are listed in Table 2.

The results of the granulometric analysis and the analysis of fractionated top soil material for the HMs contents indicated that there are some catenary patterns in the distribution of the size fractions and associated metals. The highest amounts of sand fractions were observed in subordinate sections of the catenas. This corresponds to the textural characteristics of parent material. At these positions, it is represented by sandy moraine material (catena 2) and glaciofluvial sands (catena 1). The patterns of the silt and clay fraction distribution along the slopes can be explained by the intensity of erosion–accumulation processes and, therefore, be attributed to slope morphology.

Comparison of the catenary distribution of the HMs in the particle size fractions with those in the bulk soil samples based on the analysis of L-coefficients has shown that the distribution of the HMs in the particle size fractions was less uniform than in the bulk soil material and the contrast between the dispersion and accumulation patterns in the particle size fractions was more pronounced (L coefficients ranged from 0,03–7,0). The patterns of the HMs distribution in the particle size fractions were defined by the origin of a particular size fraction and by its transformation during pedogenesis. ■

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