ISSN 1064-2293, Eurasian Soil Science, 2015, Vol. 48, No. 6, pp. 584–592. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © O.A. Samonova, A.N. Gennadiev, T.S. Koshovskii, A.P. Zhidkin, 2015, published in Pochvovedenie, 2015, No. 6, pp. 675–684.

SOIL CHEMISTRY

Metals in the Soils of a Small Watershed in the Forest-Steppe Zone of the Central Russian Upland

O. A. Samonova, A. N. Gennadiev, T. S. Koshovskii, and A. P. Zhidkin

Faculty of Geography, Moscow State University, Moscow, 119991 Russia,
e-mail: oasamonova@mail.ru, tkzv@ya.ru

Received July 21, 2014

Abstract—The spatial distributions of Mn, Cu, Ni, Co, Cr, Zn, Pb, Mo, Ti, Zr, and Fe, as well as particle sizes and humus, in the surface horizon of soils in the Lokna River small watershed (Tula oblast) have been studied. The relationships of the studied parameters have been characterized by statistical methods. Little change in particle size distribution in the humus horizons of soils is revealed from the geomorphological elements of the watershed. An increase in the content of most metals is observed in soils on the convex slopes and the bottom of the watershed balka compared to the autonomous positions. Positive correlations have been found between the contents of Co, Mn, Zr, Mo, and, to a lesser degree, Zn and Pb and the sand and coarse silt fractions; no correlations of Ni, Cr, Ti, and Fe with the particle size fractions were revealed.

Keywords: particle size fractions, humus, distribution, soils of small watersheds, autocorrelation

DOI: 10.1134/S1064229315060101

INTRODUCTION

The analysis of the soil-geochemical structure of an area is an essential component of integrated physiographic and ecological studies at different levels. The main analytical technique is catenary analysis, which involves the study of the morphological structure of representative soil-geochemical catenas and the distribution features of their chemical elements and compounds using radial and lateral differentiation coefficients.

The differentiation of total metals and their mobile compounds in different soil types and their correlation with the physicochemical properties and soil-forming processes have been studied over many decades, and the results of these studies are reported in detail [5, 8–11, 13, 18, 19–21].

The distribution of chemical elements (particularly metals) in systems more complex than catenas, e.g., in cascade landscape-geochemical systems of river basins functioning under different natural conditions, is poorly described in the literature. These studies are of applied interest: the depressions with balkas are frequently used for the discharge of pollutants, whose further behavior determines the environmental and geochemical status of the area.

Small watersheds (small landscape-geochemical arenas etc.) can be considered as elements of a higher-order cascade system: a river basin. Therefore, their geochemical parameters are essential components of the geochemical structure of the river basin. The small watersheds as integral migration systems are poorly studied in geochemical terms; only isolated reports are available [13, 15]. The lateral migration of soil solid-phase material was analyzed from the spatial distribution of spherical magnetic particles as tracers of mass transfer [3, 4]; the distribution of total metals and their mobile compounds in ravine systems was assessed [16]. Some authors [3, 16] used catenary analysis, while others [13, 15] applied the procedure involving the sampling of soils in catenas and the statistical processing of the results of chemical analysis with consideration for the geomorphological elements of the watershed.

The aims of this work were to analyze the spatial distribution of soil-geochemical parameters (particle-size fractions; humus; and total Ti, Zr, Mn, Co, Zn, Cu, Pb, Cr, Ni, and Mo) in the surface horizon of soils of a small watershed and to reveal relationships between these parameters by statistical methods.

OBJECTS AND METHODS

The small watershed of the first order (small erosional form, balka) is located in the Plavsk district of Tula oblast; it is about 1100 m long and has the main erosional form of the eastern direction of (Fig. 1). Correspondingly, the balka slopes are of the southern, eastern, northern, and intermediate exposures; there are no slopes of the western exposure, because the balka mouth (debouching into a larger form, the main balka) occurs in this part of the watershed. The balka has an irregular, unsymmetrical, teardrop shape: the watershed maximum is located at the balka head, where it reaches 800–900 m, and decreases to 300 at the approach to the mouth. The length of the water-

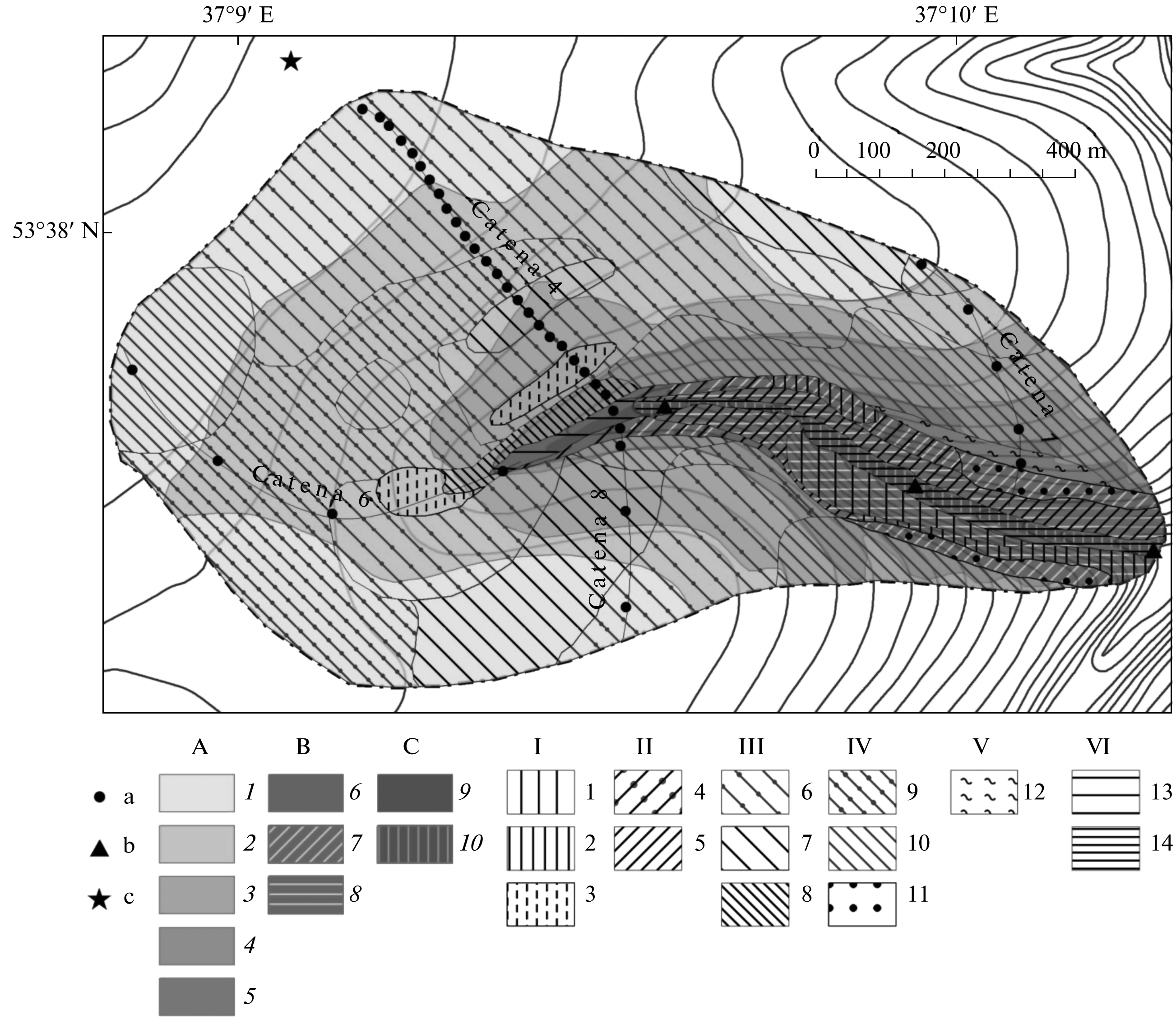

Fig. 1. Schematic map of the area under study. Geomorphological units: (A) plowed areas; (*1*) autonomous subhorizontal watershed positions, 0–1°; (*2*) upper slopes, 1–2°; (*3*) middle slopes, 2–3°; (*4*) lower slopes, 3–6°; (*5*) lower slopes, 6–12°; ((B) grassed and fallow ravine slopes; (*6*) fallow, gentle slopes, 2–3°; (*7*) fallow, steep slopes, 6–12°; (*8*) meadow, steep slopes, 5–12°; (C) ravine bottom: (*9*) fallow; (*10*) meadow, 1–3°. Sampling points: (a) catenas; (b) bottom; (c) spiral mode. Soil cover: (I) texturally differentiated soils: (1) typical gray; (2) typical and postagrogenic dark gray; (3) agrodark gray; (II) clay-illuvial chernozems: (4) shallow podzolized postagrogenic; (5) deep and very deep typical; (III) clay-illuviated agrochernozems: (6) medium-deep podzolized; (7) medium-deep typical; (8) very deep humus-stratified; (IV) dark clay-illuvial agrozems: (9) low- and medium-deep podzolized; (10) low- and medium-deep typical; (11) medium-shallow postagrogenic; (V) dark carbonate-accumulative agrozems: (12) medium-shallow mycelial; (VI) stratified soils: (13) dark-humus postagrogenic stratozems; (14) dark-humus stratozems. Solid horizontals are drawn at 2-m intervals.

shed is 1.6 km from west to east; the balka basin area is 0.96 km^2. The ravine basin is completely plowed, except the ravine itself and the adjacent steep slopes. The edge of the watershed on the slope has distinct, spatially localized boundaries, which mainly coincide with the plowland–meadow boundary.

Podzolized clay-illuvial agrochernozems (Chernic Luvic Phaeozems) are the predominant soils in the microarena; smaller areas are occupied by clay-illuvial typical agrochernozems (Luvic Anthric Chernozems), clay-illuvial typical chernozems (Luvic Chernozems) on the unplowed plots, and texturally differentiated soils: gray (Luvisols), dark gray (Greyic-Luvic Phaeozems), and agrodark gray (Greyic Luvic Anthric Phaeozems) ones; as well as clay-illuvial agrozems (Luvic Anthric Phaeozems), dark carbonate-accumulative agrozems (Anthric Phaeozems), and dark-humus stratozems on buried soil (Mollic Colluvic

Phaeozems) [7, 22]. The detailed description of the morphological profiles of the soils under study was reported earlier [3]; the soil map of the studied area is given in Fig. 1.

To study the mechanical migration of soil material within the small watershed, samples were taken from the plow (0- to 25-cm) horizon in four catenas established along the maximum height gradients from several watershed positions to the ravine bottom: 38 samples were taken in the catenas; 5 samples were taken on the bottom, and 10 samples were taken on the watershed surface. Thus, samples were taken from podzolized clay-illuvial agrochernozems (26 samples), clay-illuvial typical agrochernozems (12 samples), dark gray soils (2 samples), clay-illuvial agrozems (8 samples), and dark-humus stratozems (5 samples).

For 53 samples from the surface horizons of soils, particle size analysis was performed by the pyrophosphate method in the chemical laboratory of the Institute of Geography, Russian Academy of Sciences (Moscow). The contents of Mn, Cu, Ni, Co, Cr, Zn, Pb, Mo, Ti, Zr, and Fe were determined by atomic emission spectroscopy on a DFS-458 spectrograph in the Bronnitsa geological-geochemical expedition of the Institute of Mineralogy, Geochemistry, and Crystallochemistry of Rare Elements. The content of humus was determined by the Tyurin method with the spectrophotometric detection by the Orlov–Grindel method in the chemical laboratory of the Faculty of Geography, Moscow State University. The sample sets for the statistical processing were composed in accordance with the geomorphological elements of the small watershed: autonomous subhorizontal, transeluvial with different slopes, and transaccumulative (bottom) ones.

For particle size fractions, total metals, and humus, the main statistical parameters were calculated: mean, standard deviation, and variation coefficient. The conformity of the obtained sample set to the normal law was tested using the Kolmogorov–Smirnov and Shapiro–Wilk tests [12]. If the hypothesis about the insignificant differences from the normal law was accepted, the sample sets were compared using analysis of variance; otherwise, nonparametric criteria (Mann–Whitney and Kruskal tests) were used. In the sample sets under study, the distributions of Mn ($P = 0.44$ for the Shapiro–Wilk test), Pb ($P = 0.41$), Ni ($P = 0.19$), Cr ($P = 0.15$), and Co ($P = 0.06$) corresponded to the normal law with a significance level of 0.05. The Kolmogorov–Smirnov test was significant for the distributions of Zr, Ti, Mn, Cr, Ni, Co, and Pb ($P > 0.2$). The distributions of Mo, Zn, and Fe in the studied samples did not follow this law.

The relationship between the chemical composition and the particle size distribution in the balka soils was assessed using the Pearson's linear correlation coefficient; the presence or absence of linear spatial trends in the variation of chemical and particle-size parameters along the ravine bottom was assessed using the Spearman correlation coefficient. The tests were considered significant for the confidence probability $P = 0.95$ (clear spatial trends, significant correlation of parameters, probabilities of statistical hypotheses). Cluster analysis for combining the groups of elements with similar behaviors in soils of the landscapes studied was performed using the metric $1 - r$ (where r is the Pearson's correlation coefficient) and the complete linkage rule.

The lateral differentiation of metals in the particle-size fractions of soils in elementary landscapes of the small watershed was assessed using the lateral differentiation coefficient (L), which is equal to the ratio between the mean content of an element in the given sample set (transeluvial, bottom) and its content in the soils of autonomous (subhorizontal) landscapes.

RESULTS AND DISCUSSION

Particle size distribution. The humus and agrohumus horizons of the watershed soils have a heavy, coarse-silty loamy texture (Table 1). The distribution of particle-size fractions among the geomorphological elements of the small watershed is of low contrast. The content of fine silt decreases and the contents of the fine-sand and clay fraction increase on the slopes compared to the autonomous positions; a low accumulation of the coarse and medium sand and coarse silt fractions, as well as the dispersion of the fine silt fraction, is observed in the ravine bottom. The content of the clay fraction is maximum on the steeper, grassed, and lower slopes of the ravine. These trends can be related to the removal of the fine fractions as suspensions in the areas with intense surface water flows and their accumulation on the grassed slopes.

Significant variations in the content of particle size fractions in the surface horizon are traced along the balka bottom from the heads to the mouth: the content of the sand fraction increases to the balka mouth; the content of fine silt slightly decreases (Fig. 2). An increase in the content of the clay fraction is observed, when the balka bottom is enlarged and the slopes decrease.

Humus. The distribution of humus in the plow horizons of the small watershed soils is uniform. The contents of humus in the autonomous watershed and gently sloped trans-eluvial positions are close to its average content in the watershed. The highest values are typical for the soils in the balka bottom. In the soils of steep slopes, the content of humus significantly decreases, as well as the variation of its value.

Metals. The average contents of metals in the surface layer of the small watershed soils were calculated for the sample sets collected according to their belonging to separate geomorphological elements of the small watershed; the total set was also formed. The differences between our data and the results of other authors [1, 2, 5, 6, 11] were differentiated with respect to the elements. For all metals, except Ti and Zr, they almost completely coincide with the data from some

Table 1. The mean contents (m) of particle size fractions, humus, and metals in the humus horizon of soils on the geomorphological elements of the small watershed (V is the coefficient of correlation)

Parameter	Autonomous, <1°, n = 20		Transeluvial, slope segments						Transaccumulative, bottom, 1°–2°, n = 9		Total sample set, n = 53	
			upper, 1°–2°, n = 12		middle, 2°–3°, n = 8		lower, 3°–12°, n = 4					
	m	V	m	V	m	V	m	V	m	V	m	V
Particle size fraction (mm), %												
1–0.25	0.06	38.4	0.04	36.2	0.07	81.8	0.06	44.1	0.11	176.0	0.07	249.8
0.25–0.05	0.14	56.1	0.20	84.7	0.11	98.4	0.07	45.8	0.12	193.2	0.13	231.0
0.05–0.01	45.0	2.2	44.1	3.2	44.6	2.4	44.5	5.2	45.6	10.3	44.7	6.4
0.01–0.005	11.9	9.0	12.6	8.3	11.8	9.0	11.0	15.1	12.3	9.1	12.0	9.4
0.005–0.001	16.4	11.7	15.5	5.8	16.0	10.4	13.0	7.3	14.2	14.7	15.0	13.6
<0.001	26.6	8.3	27.6	3.1	27.4	8.7	31.4	2.2	27.7	15.7	28.1	10.1
Humus, %	6.00	12.4	6.15	9.0	6.28	9.4	4.54	27.7	6.51	7.3	5.90	13.2
Metal, mg/kg												
Cu	36	10.4	36	7	32	5.2	33	1.7	37	9.1	35	9.7
Zn	51	25.6	66	16.9	59	10.9	60	16.7	61	11.2	58	21
Pb	29	12.4	33	8.4	31	8.7	30	6.7	31	7.3	31	10.8
Co	14	16.6	16	8.3	17	10.2	17	5.9	16	13.1	15	14.4
Mo	2	19.3	2	24.8	2	31.8	2	0	2	20.4	2	22
Ni	33	16.7	35	10.2	33	7.8	39	9.1	36	16.3	34	14
Cr	80	15.4	86	14.7	96	6.7	86	2.4	89	19.2	86	15.1
Mn	550	15.4	586	10.6	583	7.3	543	14.1	556	13.8	564	12.8
Ti	6262	16.3	6300	17.4	7500	10.6	5633	10.7	6171	17.7	6413	16.9
Zr	534	18.7	543	11.5	551	9.4	573	8.6	531	8.7	541	13.9
Fe, %	3.6	12.3	4.2	14.2	3.6	12.2	4	0	3.8	7.1	3.8	13.3

literature source, which confirms the natural variability of metal concentrations in soils of the same type with similar textures. The use of different methods for the analysis of metals in the cited works also affects the absolute values. The concentration of Ti in the studied soils is higher than those in the analogous soils by 30–50% [11] and the Clark lithosphere by 50–70% [2]; the contents of Zr and Pb exceed their soil clarkes by 2 and 3 times, respectively [1].

To determine the significance of differences among the contents of metals in the elementary landscapes of the microarena, single factor analysis of variance (ANOVA) was used. A significant dependence of element concentrations in the humus horizons of soils on their positions in different elementary landscapes was revealed for Cu, Zn, Pb, Co, Fe, and, to a lesser extent, Cr. The contents of Mo, Ni, Mn, Ti, and Zr showed no significant dependence on the position of soils in the geochemical positions of the microarena. No statistically significant differences in the contents of elements in the humus horizons were revealed between the soil varieties.

The contents of metals in the "autonomous landscapes—gentle slopes—steep slopes—lower slopes—bottom" system are poorly differentiated, but the main trends could be identified. For all the studied metals, except Cu and Mo, an increase in their contents is observed in the soils on gentle slopes compared to the autonomous positions; according to the accumulation rate, the metals form the following series (increase in percentage is given in the parentheses): Zn (29.4) > Fe (16.7) > Co (14.3) > Pb (13.7) > Mn, Ni, Cr (6–7) > Zr (1.6) > Ti (0.6). For Zn, Fe, Co, and Pb, these values exceed the coefficients of variations in the soils on gentle slopes and, hence, can be considered significant. On the steep slopes, the tendency of increasing metal content continues for Co, Cr, Ti, and Zr; the contents of Cu, Zn, Pb, Ni, Mn, and Fe decrease

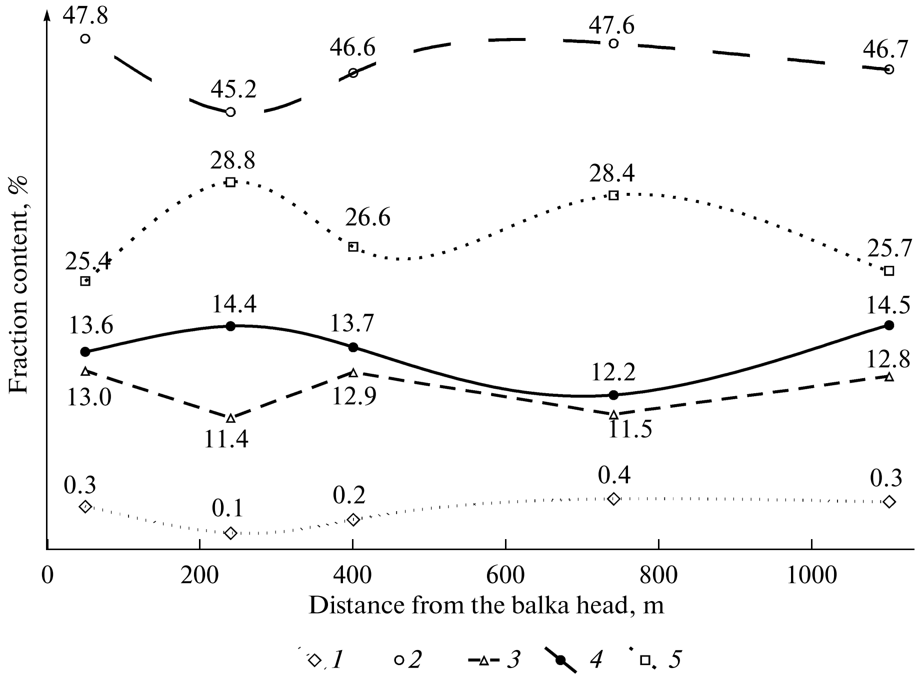

Fig. 2. Distribution of particle size fractions in soils of the balka bottom from the head to the mouth: (*1*) sand; (*2*) coarse silt; (*3*) medium silt; (*4*) fine silt; (*5*) clay.

compared to the gentle slopes. The comparison of the metal contents in the autonomous soils and those in the balka bottom indicates their increase in the latter case for all metals except Mo, Ti, and Zr. The corresponding series is as follows: Zn (19.6) > Co (14.3) > Cr (11.3) > Ni (9.0) > Pb (6.8) > Fe (5.5) > Cu (2.7) > Mn (1.0). Thus, the tendency of metal accumulation on the gentle slope is more manifested than in the bottom. This can be related to the decrease in the velocity of mechanic migration on the convex (gentle) part of the slope and the low increase in the content of clay and fine sand particles, which results in an increase in the contents of most of the studied metals. In the watershed bottom, where the soil material brought from the slopes not only accumulates, but also migrates from the heads to the mouth, the accumulative effect for metals is less manifested than on the gentle slopes.

An increase in the contents of Zr and Ti is observed along the balka bottom, from the head to the mouth (Fig. 3), which correlates with the distribution of the sand fraction containing weathering-resistant minerals (zircon, ilmenite) [17]. The dispersion of Mn, Ni, and, to a lesser degree, Cr is also observed, which can be related to the distribution of the silt fractions (Fig. 2).

The low-contrast lateral differentiation of metals in the soils among the geomorphological elements of the watershed is due to the uniformity of redox and alkali–acid conditions within the watershed. The neutral or weakly alkaline reaction of soil solution in the humus horizons of soils determines the predominance of insoluble metal forms.

The maximum variation of metal contents is revealed in the soils of autonomous landscapes (gentle slopes of the interfluve), and the minimum variation is observed on the steep slopes, at their feet. This can be related to the lower variability of the fine silt and clay fractions in the soil material at the slope foot.

The thorough testing of soils in catena 4 sampled with an interval of 25 m allowed for assessment of the natural spatial variability of metals in this cascade landscape-geochemical system. The high-frequency testing makes it possible to reveal the character (smooth or stepwise) of transitions between elementary landscapes and to determine the relationship between the metal contents and the spatial position of the soil (Fig. 4).

The variability of metals in the catena was assessed using autocorrelation functions [12]. The shift of the spatial series was assessed against the autonomous position. The obtained correlograms indicate high values of the autocorrelation coefficient up to the 15th lag for Co, Zn, Pb, and Cr (Figs. 5a, 5b) and a smooth change of the coefficient. This points to a significant role of the geomorphological factor (position in the catena) on the content of the above elements; their distribution cannot be described only by the random variation (natural variability or analytical error). A significant coefficient of correlation between the element content and the slope steepness is typical only for Co; there is no clear correlation between this parameter

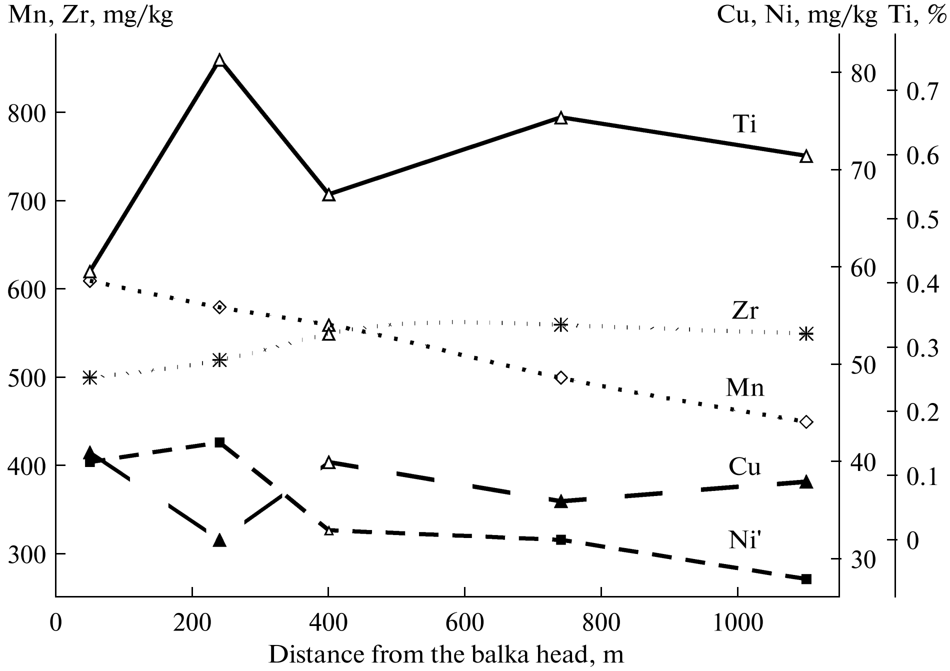

Fig. 3. Distributions of some metals in soils of the balka bottom from the head to the mouth.

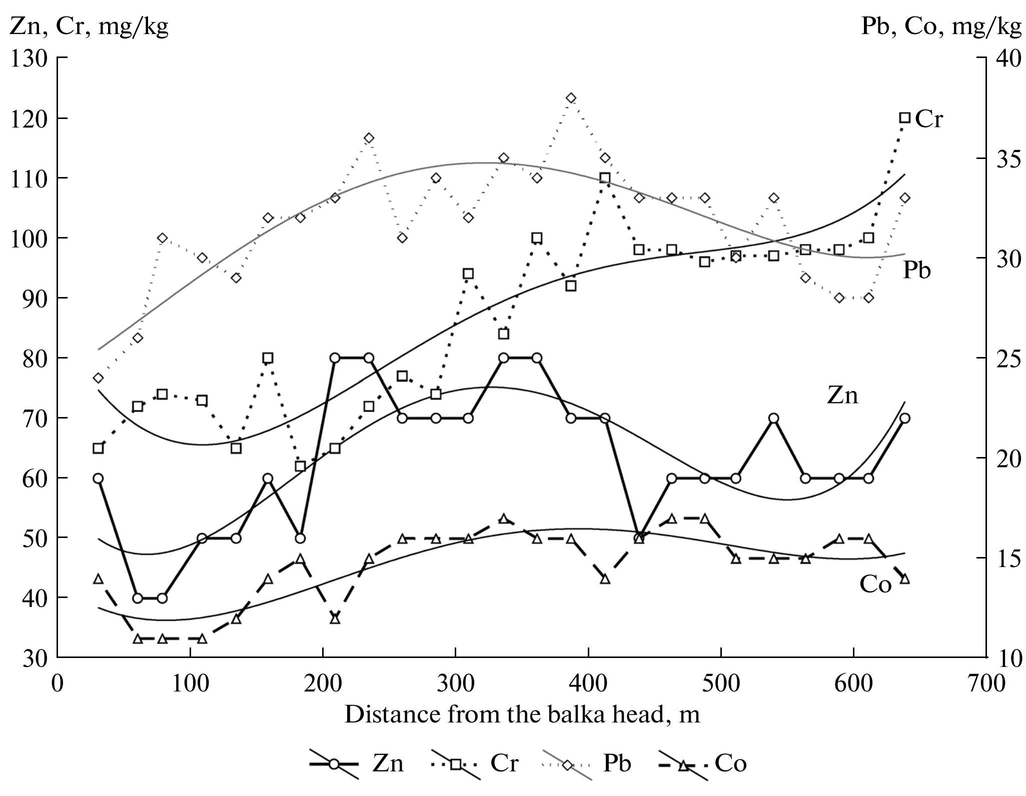

Fig. 4. Distributions of some metals in the plow horizons of soils along catena 4 (from the watershed to the ravine).

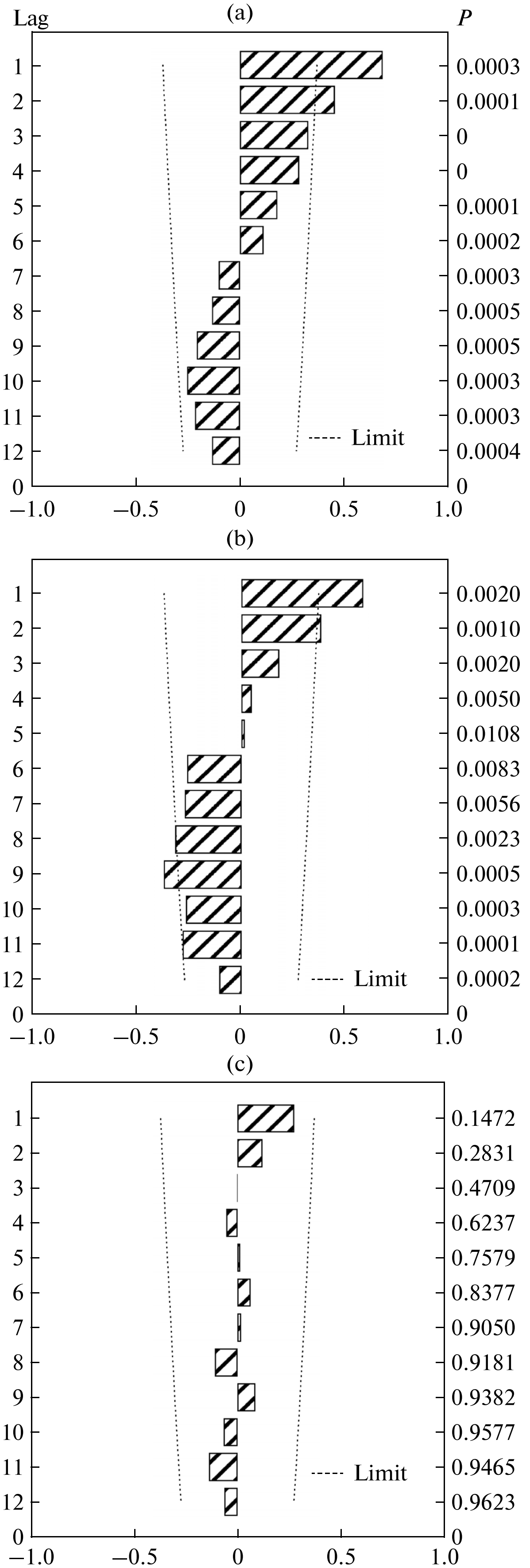

Fig. 5. Autocorrelation functions for the contents of metals in catena 4: (a) Co; (b) Zn; (c) Ni. The abscissa is the autocorrelation coefficient; (*P*) the significance level of the Ljung–Box test.

and the contents of the other elements. The contents of metals in the soils of associated landscapes vary gradually. For Ni (Fig. 5c), Ti, Cu, Mo, and Zr, the spatial series has no statistically significant autocorrelation coefficients, which indicates the absence of relationship between their contents and the position of soil in the catena.

Metal groups. Correlation analysis revealed a group of elements (Co, Mn, Zr, and Mo) having a significant positive correlation with the sand and coarse silt fractions (Table 2); the fine sand fraction also contains Pb, and the coarse silt fraction contains Zn. The grouping of such geochemically different elements as Co, Mn (geochemical analogues), and Zr (which mainly occurs in the mineral form) with Mo can indicate the deciding role of mechanical migration in the redistribution of these elements in the system under study.

A looser (although statistically significant at P = 0.95) positive correlation is traced between the content of medium silt and Cu. All these elements show a significant negative correlation with the clay fraction, as was also observed in the surface horizon of soils in a small watershed (ravine) in the middle part of the Protva River basin [13]. No correlations of Ni, Cr, Ti, and Fe with different particle size fractions were found.

The calculation of pair correlation coefficients showed a close positive correlation with the position of soil in the relief for Zn, Mn, and Co; correlation with the slope value was found only for Co.

From the results of the cluster analysis, the effect of the geomorphological factor on the grouping of metals in soils was assessed (Table 3). A single group (Mn, Ti) was formed in the autonomous soils, which unites them with steep slopes. The correlation of these elements was also revealed in soddy-podzolic soils [14]. The gentle and steep slopes and the bottom also have a common group (Ti, Cr). The total set and the bottom have two common groups: (Mo, Zr) and (Ti, Cr). The obtained results suggest that the total set is most representative for assessing the relationships between the metals in soils, because it reflects the interaction of migration processes in the area.

CONCLUSIONS

(1) Particle size distribution in the humus horizons of soils varies little among the geomorphological elements of the small watershed in the Lokna River basin (Tula oblast). On the slopes of relatively autonomous positions, the content of fine silt decreases and those of the fine sand and clay fractions slightly increase; in the bottom, a low accumulation of the coarse and medium sand and coarse silt fractions, as well as the

Table 2. Correlations of metals with particle-size fractions in the surface horizons of soils of the small watershed

Particle size fraction, mm	Elements and coefficients of correlation with the particle size fraction
1.0–0.25 (coarse and medium sand)	$Co_{0.8} > Mn_{0.7} >$ Zr, $Mo_{0.4}$*
0.25–0.05 (fine sand)	$Co_{0.8} > Mn_{0.7} >$ Zr, $Mo_{0.4} > Pb_{0.3}$
0.05–0.01 (coarse silt)	$Mn_{0.5} >$ Co, $Zr_{0.4} >$ Zn, $Mo_{0.3}$
0.01–0.005 (medium silt)	$Cu_{0.3}$
0.005–0.001 (fine silt)	$Co_{-0.4}$
<0.001 (clay)	$Mn_{-0.5} >$ Zr, $Mo_{-0.4} >$ Cu, Zn, $Co_{-0.3}$

* The correlation coefficients significant at $P = 0.95$ are shown. A minus sign before the number indicates a negative correlation.

Table 3. Groups of metals in the soils of the geomorphological elements of the small watershed

Geomorphological elements	Metal groups
Watershed area, $n = 20$	Co, Ni, $Fe_{0.69–0.85}$; Zn, $Cu_{0.61}$; **Mn, Ti**, $Zr_{0.51–0.64}$
Gentle slopes, $n = 15$	Co, Ni, $Zr_{0.62}$; **Ti, Cr**$_{0.57}$
Steep slopes, $n = 9$	**Mn, Ti, Cr**$_{0.73}$; Fe, $Cu_{0.73}$
Bottom, $n = 9$	Fe, $Pb_{0.93}$; Mn, $Ni_{0.92}$; **Mo, Zr**$_{0.78}$; **Ti, Cr**$_{0.82}$
Total sample set, $n = 53$	**Mo, Zr,** Mn, $Co_{0.34–0.65}$; **Ti, Cr**$_{0.49}$; Fe, Ni, $Pb_{0.28–0.46}$; Pb, $Zn_{0.49}$

The subscripts indicate the coefficients of correlation between the elements, characterizing the closeness of relationship; n is the number of samples. The groups of metals repeating in the soils of different geomorphological positions are typed bold.

dispersion of the fine silt fraction, is observed. The maximum concentration of clay fractions is found on the grassy slopes.

(2) An increase in the content of sand in the soil is traced along the balka bottom, from the head to the mouth. No clear distribution trends are revealed for the other fractions.

(3) According to the single factor analysis of variance, a significant correlation with the soil position on the geomorphological element of the watershed exists for Cu, Zn, Pb, Co, Fe, and, to a lesser degree, Cr, in the humus horizons of soil; for Mo, Ni, Mn, Ti, and Zr, such correlation is statistically insignificant.

(4) Higher contents of Mn, Ni, Co, Cr, Zn, Pb, Ti, Zr, and Fe are found in the soils of the upper gentle slopes compared to the autonomous soils. Accumulation of Mn, Ni, Co, Cr, Zn, Pb, and Fe is observed in the bottom soils, although less significant than on the above parts of slopes, which can be related to the intensive migration of material from the balka head to its mouth.

(5) An increase in the contents of Zr and Ti is observed along the balka bottom, from the head to the mouth, which coincides with the trend in the distribution of sand fractions; the distribution of Mn, Ni, and, to a lesser degree, Cr, whose behavior is related to the distribution of fine silt, is also observed.

(6) From the correlation analysis data (total sample set), the distributions of Co, Mn, Zr, Mo, and, to a lesser degree, Zn and Pb, are related to the sand and coarse silt fractions more actively participating in mechanical migration than the fine fractions. No correlation with particle size fractions is found for Ni, Cr, Ti, and Fe.

(7) The poor lateral differentiation of particle size, humus, and metals in soils of the watershed is due to the low slopes of its geomorphological elements and, hence, the moderate intensity of mechanical migration. The physicochemical migration of metals is also slightly manifested, because it occurs under uniform redox and alkali–acid conditions, whose parameters determine the predominance of their insoluble forms.

ACKNOWLEDGMENTS

Chemicoanalytical and field studies were supported in part by the Russian Ministry of Sciences (project no. NSh-1689.2014.5) and the Russian Foundation for Basic Research (project no. 13-05-00098).

REFERENCES

1. A. P. Vinogradov, *Geochemistry of Rare and Trace Elements in Soils* (Moscow, 1957) [in Russian].
2. A. P. Vinogradov, "Average concentration of chemical elements in the main types of igneous rocks of the Earth's crust," Geokhimiya, No. 7, 555-571 (1962).
3. A. N. Gennadiev, T. S. Koshovskii, A. P. Zhidkin, and R. G. Kovach, "Lateral migration of soil solid-phase material within a landscape-geochemical arena detected using the magnetic tracer method," Eurasian Soil Sci. **46** (10), 983-993 (2013). doi: 10.7868/S0032180X13100043
4. V. N. Golosov, A. N. Gennadiev, M. V. Markelov, A. P. Zhidkin, R. G. Kovach, K. R. Olson, and Y. G. Chendev, "Spatial and temporal features of soil erosion in the forest-steppe zone of the East European Plain," Eurasian Soil Sci. **44** (7), 794-801 (2011).
5. L. M. Dmitrakov and D. L. Pinskii, "Microelemental composition of natural and technogenic fluxes in the landscapes of the central forest-steppe," Eurasian Soil Sci. **35** (12), 1327-1334 (2002).
6. B. N. Zolotareva, "Heavy metals in soils of the upper Oka River basin," Eurasian Soil Sci. **36** (2), 164-172 (2003).
7. *Classification and Diagnostics of Russian Soils* (Oikumena, Smolensk, 2004) [in Russian].
8. D. V. Ladonin, "Heavy metal compounds in soils: problems and methods of study," Eurasian Soil Sci. **35** (6), 605-613 (2002).
9. T. M. Minkina, S. S. Mandzhieva, S. N. Sushkova, D. L. Pinskii, and E. M. Antonenko, "Effect of the particle-size distribution on the adsorption of copper, lead, and zinc by Chernozemic soils of Rostov oblast," Eurasian Soil Sci. **44** (11), 1193-1200 (2011).
10. N. N. Miroshnichenko and A. V. Tertishna, "Distribution of trace elements in podzolized soils of transeluvial landscapes of the left-bank Ukrainian forest-steppe," Gruntoznavstvo **12** (1-2), 5-11 (2011).
11. N. A. Protasova and A. B. Belyaev, "Macro- and microelements in soils of the central chernozemic area and its soil-geochemical zoning," Eurasian Soil Sci. **33** (2), 177-183 (2000).
12. Yu. G. Puzachenko, *Mathematical Methods Applied in Ecological and Geographical Studies* (Akademiya, Moscow, 2004) [in Russian].
13. O. A. Samonova and E. N. Aseyeva, "Soil-geochemical differentiation of small erosion forms in the southeastern part of Smolensk-Moscow Upland," Vestn. Mosk. Univ., Ser. 5: Geogr., No. 6, 80-87 (2010).
14. O. A. Samonova, N. E. Kosheleva, and N. S. Kasimov, "Associations of microelements in sod-podzolic soil profile of southern taiga," Vestn. Mosk. Univ., Ser. 17: Pochvoved., No. 2, 14-19 (1998).
15. O. A. Samonova, N. S. Kasimov, and E. N. Aseyeva, "Mobile forms of metals in the soils of erosional landforms in the southeastern part of the Smolensk-Moscow Upland," Vestn. Mosk. Univ., Ser. 5: Geogr., No. 6, 67-75 (2011).
16. I. N. Semenkov, E. N. Aseyeva, and E. V. Terskaya, "Geochemical structure of forest-steppe catenas of a balka catchment in the Upa River basin," Vestn. Mosk. Univ., Ser. 5: Geogr., No. 6, 68-75 (2013).
17. R. W. Fitzpatrick and D. J. Chittleborough, "Titanium and zirconium minerals," in *Soil Mineralogy with Environmental Applications*, Ed. by J. B. Dixon and D. G. Schulze (Soil Scientific Society of America, Madison, WI, 2002), pp. 667-690.
18. A. Kabata-Pendias, *Trace Elements in Soils and Plants* (CRC Press, Boca Raton, FL, 2001).
19. P. Marshall and R. W. Fairbridge, *Encyclopedia of geochemistry* (Kluwer, Dordrecht, 1999).
20. T. M. Minkina, G. V. Motuzova, O. G. Nazarenko, V. S. Kryshchenko, and S. S. Mandzhieva, "Forms of heavy metal compounds in soils of the steppe zone," Eurasian Soil Sci. **41** (7), 708-716 (2008).
21. D. Sarkar, R.Datta, and R. Hannigan, *Concepts and Applications in Environmental Geochemistry* (Elsevier, Amsterdam, 2007).
22. *World Reference Base for Soil Resources 2014. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps* (Food and Agriculture Organization, Rome, 2014).

Translated by K. Pankratova