

Geochemistry of Holocene — Late Pleistocene sediments in the Berezovka River valley (Near-Yenisey Siberia)*

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Despite their great importance, Holocene — Late Pleistocene sediments are poorly studied in the valleys of rivers in the Krasnoyarsk forest-steppe territory. We present the first detailed study of the geochemical composition of the first floodplain terrace sediments in the valley of the Berezovka River, and the continuous accumulation that occurred at the Late Pleistocene — Holocene (from 20833 ± 519 cal yr BP). This is of great fundamental importance and is the basis for further studies on the influence of anthropogenic activities on the natural environment in the Krasnoyarsk agglomeration. The sediments were covered by modern alluvial dark-humus hydrometamorphosed soil. Macromorphological studies and investigation of the humus content have revealed a well-developed process of humus formation and humus accumulation, a gley process. The measured contents of some elements (U, Pr, Rb, V, Bi, Cd, As, Th, Ga, Co, and Sm) exceeded the respective Clarke values for the Earth's crust. The distribution of most elements and their accumulation in the Middle-Late Holocene (from to 5477–4985 to 1241–803 cal yr BP) in the middle of the sediment profile is explained by the high content of mud and clay minerals. Based on the coefficients of radial migration, we established that most of the studied elements were introduced into the sediments during high water levels and floods. The values of palaeomarkers indicate a change in climatic conditions in the Late Pleistocene and Holocene from dry and cold to more humid and warm, and from arid and cold (in the Early Holocene) to modern climatic conditions, respectively.

Keywords: Geochemistry of sediments, radiocarbon dating, Holocene, Late Pleistocene, Berzovka River first floodplain terrace, alluvial soils, Krasnoyarsk forest-steppe, Yenisey River basin.

1. Introduction

Terrace sediments are complex natural formations owing to the synchronous effects of geological, geomorphological, hydrological processes and soil formation. Studies of cross-sections in river valleys are relevant for both scientific and practical purposes because many human activities occur within river basins and, more specifically, within water catchment areas of large and small rivers.

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Alluvial soils in the terrace sediment profile are important parts of the biosphere. They are habitats for diverse terrestrial organisms, participate in the differentiation of the environment and biosphere, and act as a factor of biological evolution (Shimanskaya and Poznyak, 2016). Considering the particular position of the soils at the interface of the atmosphere, lithosphere, and hydrosphere, these soils are vital for both biological and geological changes. Hydromorphic soils are formed in the transition or illuvial zone and act as geochemical barriers for some compounds (Molchanova et al., 2003), thereby supporting their special roles in biological and geological cycles.

Studies on the hydrological regimes of rivers, sedimentation, geochemical features and pollution of sediments, and environmental evolution and reconstruction based on alluvial sediments have been conducted in various territories within the European part of Russia and West Siberia, and in several foreign countries (Pope and van Andel, 1984; Waters and Nordt, 1995; Liu et al., 1996; Gocht et al., 2001; Berner et al., 2012; Keen-Zebert et al., 2013; Matys Grygar et al., 2014; Olszak et al., 2019; Budko et al., 2020; Chen et al., 2020; Lombardi et al., 2020; Sheinkman et al., 2021; Vandenberghe et al., 2021). However, despite the high value of such studies, terrace and floodplain sediments, including those in the Krasnoyarsk forest-steppe area, have been poorly studied.

The aim of this study was to obtain the geochemical characteristics of the terrace sediments of the Krasnoyarsk forest-steppe area, where continuous sediment accumulation occurred at the Late Pleistocene — Holocene. This is of great fundamental importance and is the basis for further studies on the influence of anthropogenic activities on the natural environment in the Krasnoyarsk agglomeration.

2. Study area

The study area is located in the Berezovka River valley, within the Krasnoyarsk open-type piedmont forest-steppe depression (Fig. 1).

The geological framework of the territory of the Krasnoyarsk forest-steppe area consists of structures of the Salair fold (East Sayan) and the Rybinskaya (Devonian) and Chulym — Yenisey (Jurassic) depressions. The deposits developed here refer to the Upper Proterozoic (Riphean and Vendian), Cambrian, Devonian, Carboniferous, Jurassic, and Quaternary (Fig. 1, c). They are represented by various sedimentary rocks and contain both animal and plant fossils. The southeastern part of the Krasnoyarsk forest-steppe area corresponds to the northwestern spurs of the East Sayan mountain ranges, which comprised syenite intrusions and intensively dislocated sedimentary units of the Upper Proterozoic and Cambrian ages.

In terms of tectonics, the Krasnoyarsk depression is a region where the tectonic units of different natures and ages merge. The southern part is represented by the Altai — Sayan Palaeozoic fold zone, the northwestern and northern parts are occupied by the West Siberian Plate, and the northeastern and eastern parts correspond to the Precambrian Siberian Platform (Sazonov et al., 2010; Makhlaev et al., 2012).

The hydrographic network of the Krasnoyarsk depression is represented by the Yenisey River and its main tributaries (Bazaikha, Kacha, Yesaulovka, Berezovka, Karaulnaya, Buzim, and others (Fig. 1, b)). The lower part of the Yenisey River Valley is a terraced erosional and depositional plain. Its complex structure can be seen on steep and intensively cut slopes, where the upper part of the valley is replaced with gentler and smoother slopes. In terms of the geomorphology of the Krasnoyarsk depression, topographic stages

related to the terraces of the Yenisey River and interfluvies are particularly noteworthy. Yamskikh (Yamskikh, 1992) distinguished between nine terraces within the limits of the depression. In terms of structural and morphological peculiarities, these terraces were grouped into three complexes: high-level (including terraces at 120–135 (150), 90–120, and 60–80 m), medium level (35–55 m), and low-level (24–30, 15–18, 10–14, and 7–10 m) terraces (Fig. 1, c). The date for the onset of floodplain formation is 6–4 ka BP (Yamskikh, 1993; 1996; Yamskikh et al., 1999). The terraces and floodplain are mainly composed of alluvium consisting of clays, gravels, and pebblestones.

The climate of the Krasnoyarsk depression is sharply continental in nature. Climate continentality is expressed in large amplitudes of air temperature variations: the annual and diurnal air temperatures are 38 °C (based on average daily values) and 9–12 °C, respectively. The average annual temperature was positive (0.5 to 0.6 °C).

Forest vegetation (pine and birch forests) in the Krasnoyarsk depression can be found on the northern slopes of highlands, whereas poplar and willow stands can be found on the river islands. Steppe vegetation develops on the flat uplands of water divides, terraces of the Yenisey River, and on the southern and southwestern slopes of highlands. Meadow steppe occupies the non-flooded parts of river valleys and islands, as well as the southern and southwestern slopes of highlands. Swamp vegetation is insignificantly developed at sites characterised by excessive drainage moisture (within river floodplains and lake shores).

Chernozem soils are developed in forest-steppe areas (typically leached chernozems and podzolised chernozems in topographic lows). Steppe parts are characterised by common, or less frequently occurring southern chernozems. Chernozems are also developed on the terraces of the Yenisey River. The areas of birch forests, coppices, and clearings on the northern slopes of highlands in the western and northwestern parts are dominated by dark grey, grey, and light grey forest soils (Ivanova, 1976; Kirillov, 1988). Intrazonal soils in the Krasnoyarsk forest-steppe area are represented by swamp, meadow, meadow chernozem, floodplain, and skeleton (lithic) soils (Shpedt et al., 2015).

The target of our study was the Berezovka-1 (IV) section located at the first floodplain terrace of the Berezovka River (right tributary of the Yenisey River) (Figs 1–3).

The Berezovka-1 (IV) section is located on the right bank of the Berezovka River, 2.47 km south-southeast of the Zykovo setting, 19.2 km from the river mouth (55°55′ 36.69″ N, 93°09′ 34.54″ E), and 205 m above sea level. Meadow vegetation, with a predominance of gramineous and clover, is developed in this area, and willows grow in low-standing areas (Zharinova, 2011).

3. Materials and methods

During fieldwork, we conducted macromorphological descriptions of the section using the standard scheme of field studies of soils. We collected a number of sediment samples following the methodological recommendations (Ivanov and Demkin, 1996).

The grain size composition of soils and sediments was determined in the laboratory on an average sample in still water using N. A. Kachinskiy's version of the pipette method (Shein, 2009).

The total organic carbon (TOC; humus) content was determined by wet burning according to I. V. Tyurin (Ponomareva and Plotnikova, 1980). Carbonates were determined by the exchange (acidimetric) method (Arinushkina, 1970).

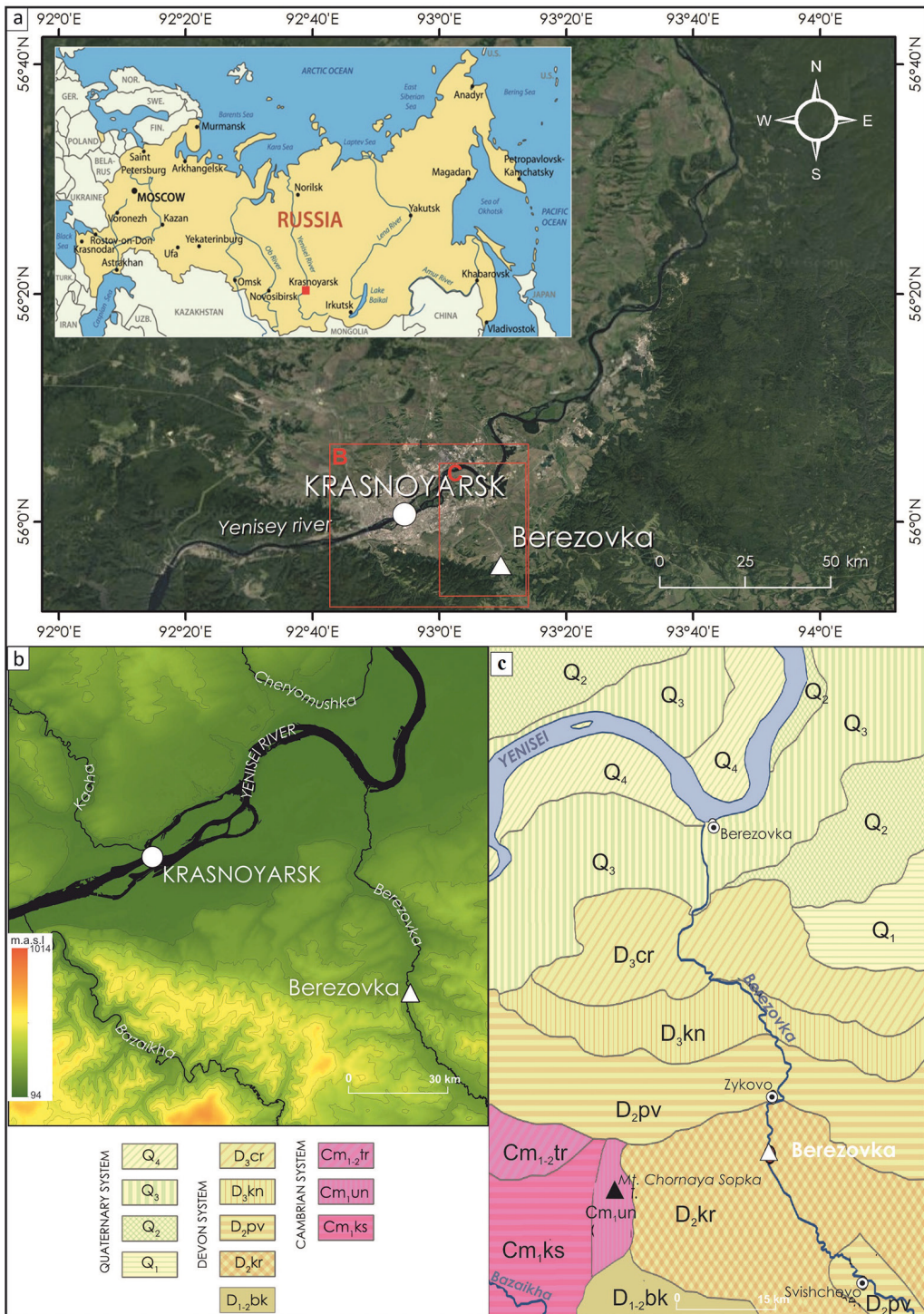




Fig. 2. View of the Berezovka River valley near the location of the Berezovka-1 (IV) section

Fig. 1. Location of the Berezovka-1 (IV) section (a); Topographic model of the study area (b); Geological map of the study area (c). Cambrian system: Cm₁ks — Koyskaya formation. Conglomerates, sandstones, quartzites, Grauvak sandstones, lime and lime-clay shales, limestones, dolomites; Cm₁un — Ungutskaya formation. Dolomites, dolomitic limestones, limestones, conglomerates; Cm_{1,2}tr — Lower and middle sections, undivided. Torgashinskaya formation. Limestone and dolomites. Devon system: D₁₋₂bk — Lower and middle sections, undivided. Byskarskaya series comprised prophyrites, diabases, orthophyrs, and their tuffs. Conglomerates, sandstones, aleurolites, marls; D₂kr — Karymovskaya formation. Large-peeled conglomerates, sandstones, aleurolites. Amygdalefir coverings; D₂pv — Pavlovskaya formation. Conglomerates, sandstones, aleurolites, limestones with chalcedony; D₃kn — Kungusskaya formation. Sandstones, marls, aleurolites; D₃cr — Charginskaya formation. Quartz sandstones, aleurolites, marls, limestones with chalcedony. Quaternary system: Q₁ — Lower section. Alluvial loams, sands, and pebbles (VII terrace of the Yenisey River); Q₂ — Middle section. Alluvial sands, pebbles, and loams (IV–VI terraces of the Yenisey River); Q₃ — Upper section. Alluvial sands and pebbles (I–III terraces of Yenisey River); Q₄ — Modern sections. Alluvial sands and pebbles of the floodplain terraces of the Yenisey River and its tributaries. Compiled by: a — on the Google Earth satellite image; b — based on the Shuttle Radar Topography Mission (SRTM); c — compiled by I. A. Weisbrot based on (Zhuiko et al., 1959)

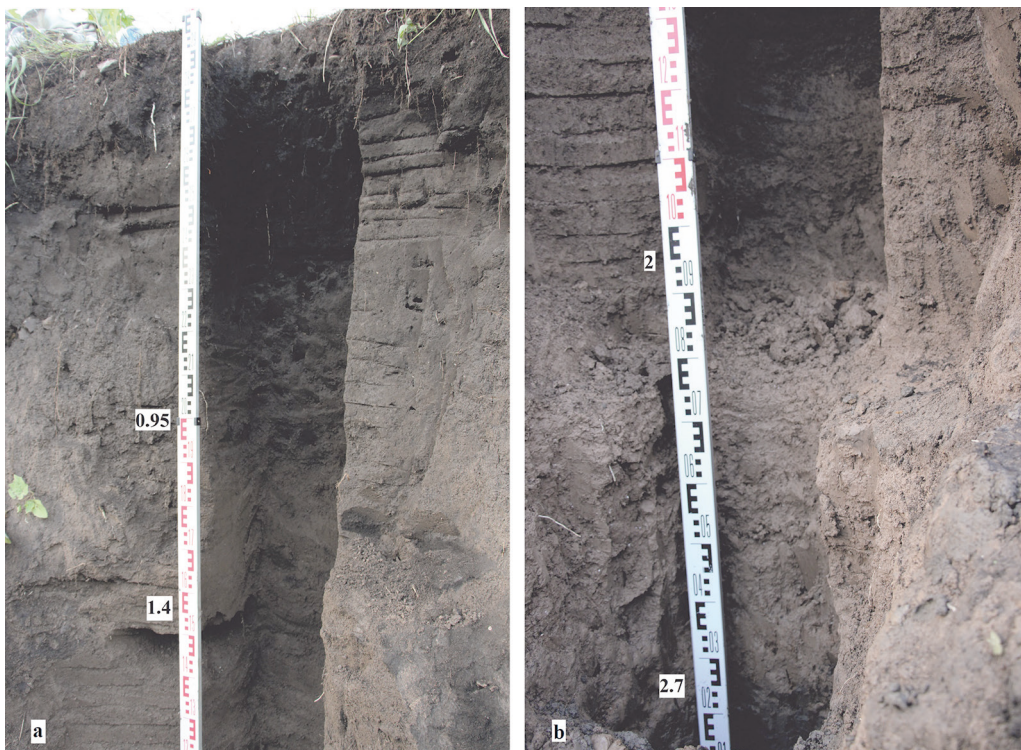


Fig. 3. First floodplain terrace sediments of the Berezovka-1 (IV) section:
a — upper; b — lower parts

The geochemical compositions of the samples were determined at the Pope John Paul II State School of Higher Education (Biala Podlaska, Poland). The samples were mineralised in a Teflon closed vessel with Suprapur chloric and nitric acids (3:1) in an Anton Paar Multi-wave PRO microwave oven under pressure control. After dilution to 50 ml, the samples were analysed using a SpectroBlue ICP-OES spectrometer. Argon gas flow: coolant flow, 12 l/min; auxiliary flow, 0.90 l/min; nebuliser flow, 0.78 l/min. A total of three measurements were conducted; the pump speed was 30 rpm. Calibration was done using Bernd Kraft Der Standard Spectro Genesis ICAL and VHGM68-1-500 Element Multi Standard 1 in 5% HNO₃.

Microscopic studies for mineral composition analysis were conducted using SEM Tescan Vega III SBH with EDS Oxford X-Act in R&D Norinickel SibFU Krasnoyarsk, Russia. The analytical conditions were as follows: an accelerating voltage of 20 kV, a beam current of 1.2 nA, and a measurement time of 120 s.

Radiocarbon dating of the bulk sediments specimens from the Berezovka-1 (IV) section was conducted at the Laboratory of Isotopic Research (Geology Centre of Common Use, Department of Geology and Geoecology, Faculty of Geography, Herzen Russian State Pedagogical University, St. Petersburg). Radiocarbon ages were calibrated using OxCal 4.4 (Bronk Ramsey, 2009). The ages are presented in calibrated years (cal yr) before present (BP; 0 yr BP=1950 AD), and uncertainties are given at the 95.4% confidence level. The upper date, reflecting the period of latest (modern) soil formation, was only calibrated at a confidence level of 68.3%.

4. Results

According to the radiocarbon dates, the studied section in the Berezovka River valley began to form $20\,833 \pm 519$ cal yr BP (Table 1). The section evolution spans the entire Late Pleistocene and Holocene.

Macromorphological studies (Shishov et al., 2004) have shown that a dark humus layer (horizon) develops in the upper part of the section. It has a predominantly dark grey colour and cloddy structure, and ranges from sandy loam to middle clay loam. The layer is compacted, has medium porosity and fissures, and is penetrated by herbaceous plant roots. This layer is most frequently fresh.

The succession of horizons in the section was marked by gradual and smooth transitions. The upper part of the profile showed that there were no clearly visible interbeds of fresh mineral material that were not involved in soil formation. Gleisation is weakly developed and can be seen only in the: 1) olive and greyish blue colour of the lower layers, and 2) presence of newly formed ferruginous units (Table 2).

In the upper part of the section, a large silt fraction was dominant (41–50 %) within the accumulative humus horizon of soil (depth of 1–69 cm), which was formed in the Late Holocene. At depths of up to 53 cm, the grain-size composition type is light clay loam and high contents of the fine sand fraction (23–34 %) are reported, while the mud content only reaches 14 %. From 53 to 69 cm, the grain-size composition type was middle clay loam and the fraction of mud increased up to 26 %. In general, in the accumulative humus horizon of soil (depth of 1–69 cm), the physical clay (particle size of less than 0.01 mm) content gradually increased from 22 % near the surface to 47 % at a depth of 69 cm.

Table 1. Results of radiocarbon dating of the first floodplain terrace deposits from the Berezovka-1 (IV) section. Calibration was made using the OxCal 4.4

Section and sampling depth from the surface (m)	Lab number	Age (14C yr BP)	Calibrated age (cal yr BP)	Median Calibrated Age (cal yr BP)
Berezovka 0.65–0.7	SPb_2446	200 ± 25	291–151* (221±70)	185
Berezovka 0.85–0.9	SPb_2447	1100 ± 70	1241–803 (1022 ± 219)	1016
Berezovka 1.45–1.5	SPb_2448	4592 ± 70	5477–4985 (5231 ± 246)	5295
Berezovka 2.05–2.1	SPb_2449	7970 ± 70	9005–8605 (8805 ± 200)	8826
Berezovka 2.45–2.5	SPb_2450	$11\,440 \pm 200$	13758–12930 (13344 ± 414)	13329
Berezovka 2.65–2.7	SPb_2451	$17\,189 \pm 200$	21352–20314 (20833 ± 519)	20754

* The upper date, which reflects the latest (modern) period of soil formation, is calibrated only within 68.3 % of the probability. For the rest of the data, intervals of 95.4 % probability were used.

Table 2. Macromorphological structure of the Berezovka-1 (IV) section

Age	Depth, cm	Horizon description
Late Holocene	0–1	Moist ground litter of grasses and tree waste
	1–33	Fresh compacted dark grey light clay loam (whitish tarnish forms when drying); cloddy-nutty structure; middle pores and middle fissures; penetrated with a dense network of herbaceous plants' roots; gradual colour transition, blurred boundary
	33–53	Fresh light dense dark grey clay loam (whitish tarnish forms when drying); cloddy-nutty structure; middle pores and middle fissures; penetrated with a dense network of herbaceous plants' roots; gradual colour transition, blurred boundary
	53–69	Fresh compacted heavy dark-grey clay loam (whitish tarnish forms when drying); cloddy-nutty structure, compacted; middle pores and middle fissures; penetrated with a dense network of herbaceous plants' roots; gradual colour transition, blurred boundary
	69–95	Fresh loose brownish grey light clay; cloddy-nutty structure; large pores and large fissures; penetrated with a dense network of herbaceous plants' roots; gradual colour transition, indistinct (blurred) boundary
	95–112	Light compacted brown (with dark grey spots) clay; cloddy structure; middle pores and middle fissures; penetrated with a dense network of herbaceous plants' roots; violent effervescence with HCl; gradual colour transition, blurred boundary
	112–137	Fresh compacted light dark brown and greyish clay; nutty structure; middle pores and middle fissures; penetrated with a moderately dense network of herbaceous plants' roots; violent effervescence with HCl; gradual colour transition, blurred boundary
Mid-Holocene	137–157	Brown heavy fresh clay loam with whitish tarnish; fine cloddy-nutty, poorly expressed, loose structure; large pores and large fissures; penetrated with a moderately dense network of herbaceous plants' roots; violent effervescence with HCl; gradual colour transition, blurred boundary
	157–200	Moist compacted heavy brown clay loam; large cloddy structure; middle pores and middle fissures; penetrated with a moderately dense network of herbaceous plants' roots; violent effervescence with HCl; gradual colour transition, blurred boundary
Early Holocene	200–239	Moist firm heavy light brown (with a fulvous tone) clay loam; poorly expressed structure; fine pores and fine fissures; singular plant roots; violent effervescence with HCl; extends to the water level
Late Pleistocene	239–270	Moist light brown (with a fulvous tone) heavy clay loam; poorly expressed structure; fine pores and fine fissures; singular plant roots; violent effervescence with HCl
	270–300	Greyish blue clayey sediments
	300–330	Brown sandy sediments with fulvous interbeds and coal inclusions (1–2 mm), transiting to pebblestone

In the sediments occurring at depths of 69–137 cm (accumulative humus horizon with hydrometamorphic features), which were dated back to the Late Holocene, the grain-size composition type was light clay and the mud fraction was dominant (40%). The large silt content was high (28–36%) throughout this layer, whereas a higher fine silt content (22%) was reported at a depth of 69–95 cm. Physical clay distribution was uniform within this layer, and its content was 61–65%.

The layers at depths of 137–239 cm, formed in Mid- and Early Holocene, have heavy clay loam grain-size composition. They demonstrated a high content of large silt and mud

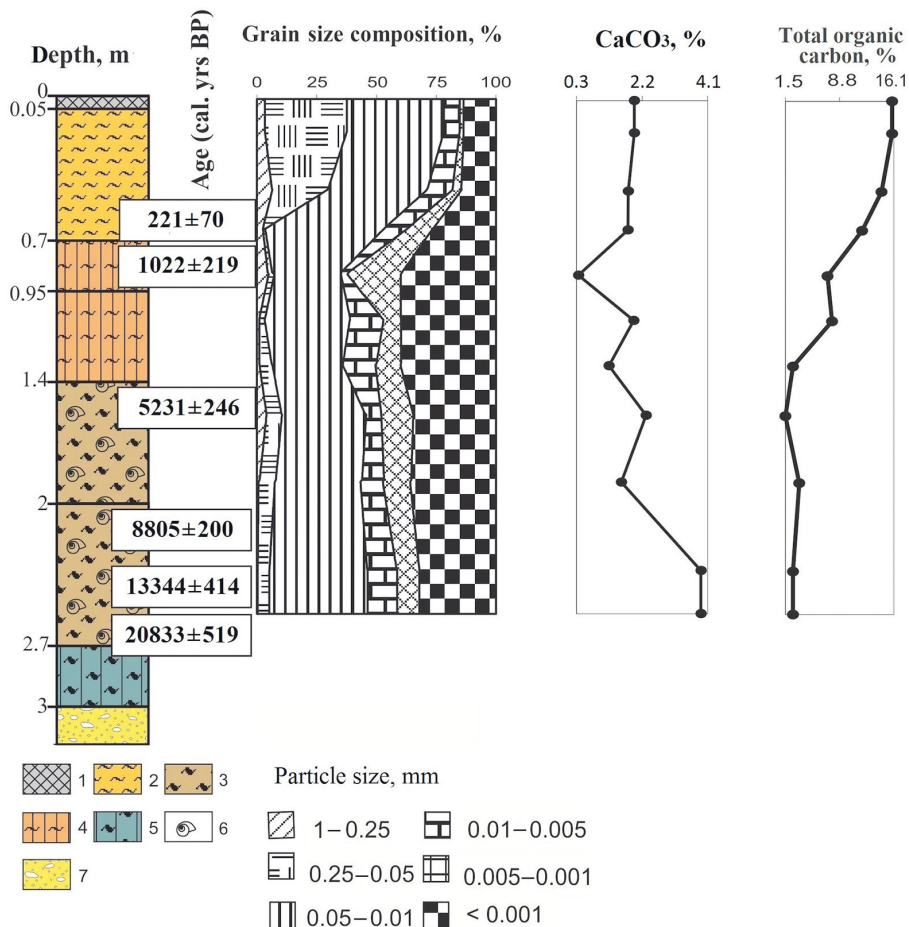


Fig. 4. Grain-size composition, CaCO₃ distribution, and total organic carbon (TOC) in the Berezovka-1 (IV) section:

1 — soil; 2 — light clay loam; 3 — heavy clay loam; 4 — clay; 5 — greyish blue clay; 6 — mollusc shells; 7 — sandy-pebble sediments

fractions (32–41 %); an increase in the large silt fraction and a decrease in the mud content are reported in the lower part of this interval. Physical clay distribution within this interval was uniform (54–57 %).

In general, the distribution of size fractions along the section is irregular; an increased content of physical clay is observed at the 69–137 cm interval, and an insignificant decrease is observed at depths of 137–239 cm. The grain size composition of the section ranged from light clay loam to light clay (Fig. 4, Table 3).

The carbonate content in the profile was found to vary from very low to low (0.4–3.9 %). Its minimum value was observed in the Late Holocene horizons at depths of 69–95 cm, while its maximum value was observed in the Early Holocene horizons at depths of 200–239 cm (Fig. 4, Table 4).

The thickness of the accumulative humus horizon in alluvial dark humus hydrometamorphosed soil of the Berezovka-1(IV) section was 69 cm, and it was formed during the

Table 3. Grain-size composition of sediments from the Berezovka-1 (IV) section, %

Age	Depth, cm	Grain size, mm							Grain-size composition
		1-0.25	0.25-0.05	0.05-0.01	0.01-0.005	0.005-0.001	<0.001	<0.01 (physical clay)	
Late Holocene	1-33	3	34	41	7	2	13	22	Light clay loam
	33-53	7	23	42	11	4	14	29	Light clay loam
	53-69	3	1	50	10	11	26	47	Middle clay loam
	69-95	5	2	28	3	22	40	65	Light clay
	95-112	1	2	36	14	7	40	61	Light clay
	112-137	1	5	29	14	11	40	64	Light clay
Mid-Holocene	137-157	4	6	35	6	13	35	54	Heavy clay loam
	157-200	1	7	36	9	11	36	57	Heavy clay loam
Early Holocene	200-239	0	5	41	12	9	32	54	Heavy clay loam

Table 4. Carbonate and total organic carbon content in the Berezovka-1 (IV) section

Age	Depth, cm	CaCO ₃ , %	Total organic carbon (TOC), %
Late Holocene	1-33	2.0	15.9
	33-53	1.8	14.4
	53-69	1.8	11.8
	69-95	0.4	7.2
	95-112	2.0	7.8
	112-137	1.2	2.5
Mid-Holocene	137-157	2.3	1.5
	157-200	1.6	3.4
Early Holocene	200-239	3.9	2.5

late Holocene (291–151 cal yr BP). The TOC content in the accumulative humus horizon is very high (up to 15.9%). The distribution of TOC content across the profile did not show any sharp fluctuations, and a general gradual decrease was observed in the TOC content with depth, showing slight fluctuations in the lower part (Fig. 4, Table 4).

Major elements in the studied section are Al (4.3%), Fe (3.6%), Ca (2.4%), Mg (1.1%), K (0.5%), Na (0.1%), P (0.1%), and Mn (0.08%). However, A. I. Perelman suggests (Perelman and Kasimov, 1999; Alekseenko et al., 2018) that the threshold content for dividing major and trace elements is $1 \cdot 10^{-2}\%$. Therefore, the list of major elements also included Rb (0.05%), Ba (0.02%), V (0.02%), U (0.02%), Sr (0.013%), and Pr (0.011%). The other elements measured are referred to as trace elements: Zn, Cr, Nd, Co, Ni, Ce, Ga, Li, La, Cu, Th, Pb, Y, As, Sm, Bi, and Cd. Their average contents in the

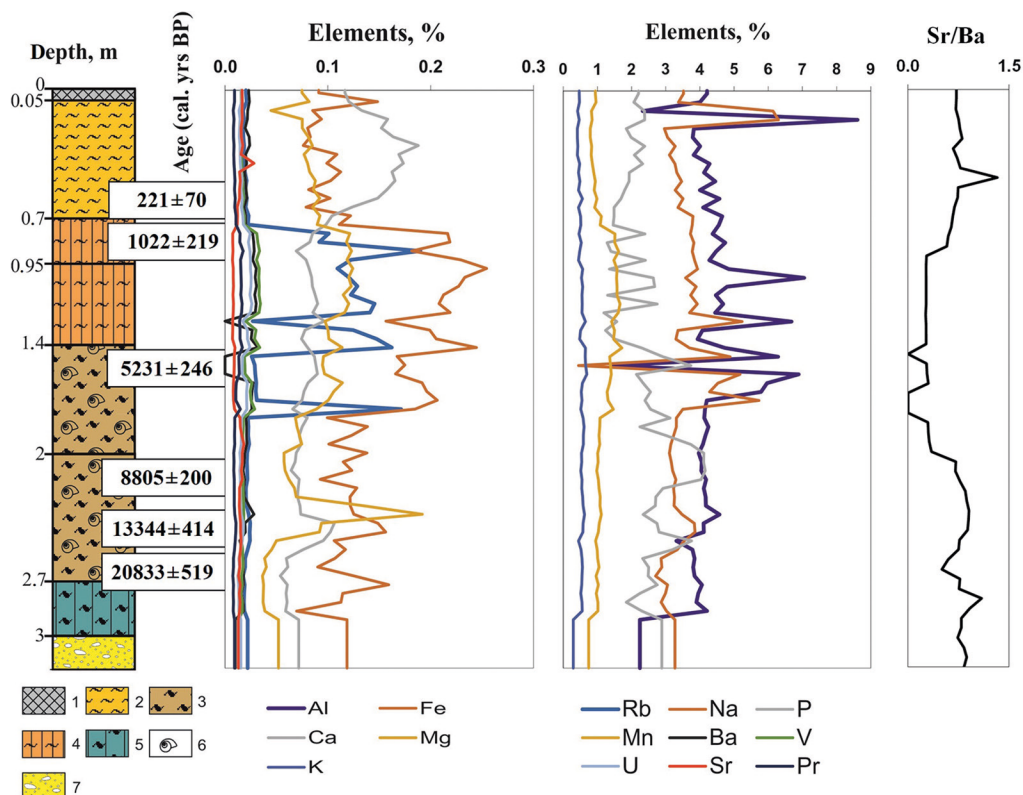


Fig. 5. Major element and Sr/Ba distribution in the Berezovka-1 (IV) section:

1 — soil; 2 — light clay loam; 3 — heavy clay loam; 4 — clay; 5 — greyish blue clay; 6 — mollusc shells; 7 — sandy-pebble sediments

profile range from 0.1 to 0.0001 %. The concentrations of Yb and Se were below detection limit (10^{-8} %; Figs 5 and 6).

We calculated the coefficients of the concentrations (C_c ; ratio of the average content of an element in the Berezovka-1(IV) section to its Clarke value in the Earth's crust) by comparing the average element contents along the profile with Clarke values (relative abundances of chemical elements) for the Earth's crust (Vinogradov, 1962; Alekseenko and Alekseenko, 2013). This coefficient facilitates the assessment of the accumulation of chemical elements in a research area compared to the global background. The following major components can be distinguished for the section elements: U ($C_c = 70$), Pr (12), Rb (3), and V (2). The level of accumulation caused a significant increase in the enrichment factor. Among the trace elements, such an exceedance is characteristic of Bi (1943), Cd (31), As (17), Th (2), Ga (2), Co (2), and Sm (1.2). The C_c s of these elements for the entire profile generally exceeded 1; a significant peak was observed for Bi, whose content exceeded the crustal Clarke value by several orders of magnitude. The series of elements in the order of increasing C_c number is: $Sm < Th < Ga < Co < V < Rb < Pr < As < Cd < U < Bi$.

Bismuth is one of the most poorly studied elements in the Earth's crust. The difference between its Clarke estimates by different authors is 19-fold: A. P. Vinogradov suggests it to be $9 \cdot 10^{-7}$ %, while C. P. Taylor estimates it as $1.7 \cdot 10^{-5}$ % (Vinogradov, 1962;

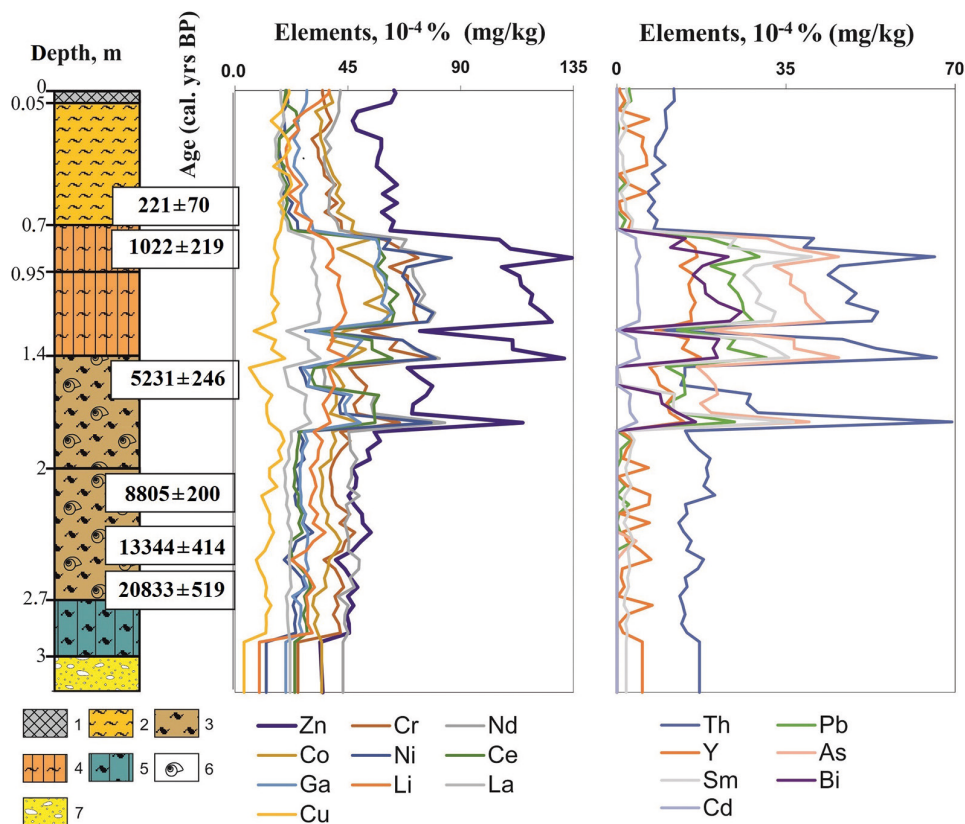


Fig. 6. Trace element distribution in the Berezovka-1 (IV) section:

1 — soil; 2 — light clay loam; 3 — heavy clay loam; 4 — clay; 5 — greyish blue clay; 6 — mollusc shells; 7 — sandy-pebble sediments

Taylor, 1964; Perelman and Kasimov, 1999). Notably, bismuth is a rare element, but not a disseminated one, and has a good mineral-forming ability. According to Goldschmidt (Goldschmidt, 1923; Perelman and Kasimov, 1999), bismuth is a chalcophile element.

Bismuth usually forms sulphides; however, it can also occur in the form of: oxides, tellurides, selenides, carbonates, and as inclusions in other minerals. The presence of bismuth minerals might be related to contact metamorphism, which is additionally supported by syenite intrusions identified in the surrounding rocks. However, the supposedly high Bi content in sulphides has not been justified by the results of electron microscopy because sulphides were not found. Conversely, bismuth is bound to mineral phases in soils, mostly iron oxides (Manaka, 2006), clay minerals, and organic matter (Murata, 2010). According to Murata, bismuth is dependent on many different factors, such as dissolved organic matter, humic acids, pH, and the precipitation of bicarbonates or hydroxides.

Uranium was found in xenotime; additionally, uranium may be contained in monazite and zircon in amounts close to the error level. Cadmium can be present as an admixture of sulphides. No arsenic was found in the minerals; however, it may be present in amounts close to the error level in extremely abundant iron minerals in the studied samples. Praseodymium is found in phosphates and other rare-earth element minerals.

Examination of the mineral composition using scanning electron microscopy (SEM) with detector EDS revealed the following phases: hornblendes (including tremolite and actinolite), feldspars (from orthoclase to Labrador spar-bytownite), iron oxides and/or hydroxides (magnetite, haematite, and goethite), Ti-Fe phases of varying compositions, Fe-Mn phases, sphene, rubinite, Fe-axinite, almandine, muscovite, quartz, zircon, baddeleyite, apatite, montmorillonite, kaolinite, calcite, portlandite, native zinc, and micas. We also revealed the mineral groups that corresponded to the compositions of the identified phases, but the element proportions did not fit any following mineral: chlorite, pyroxenes (including enstatite), and tourmaline (including elbaite and dravite).

Rare-earth minerals are represented by phosphates (monazite and xenotime), heulandite, and aluminosilicate, which is similar to Fe-axinite. Monazite was the most frequently found mineral.

The abundance of feldspars, hornblendes, and pyroxenes, together with the high amounts of Ti- and Fe-containing minerals, indicates that sediments in the Berezovka River first floodplain terrace were disintegration products of mafic rocks.

The general distribution of elements along the profile showed abrupt increases in the contents of most studied elements in the accumulative humus horizon with hydrometamorphic features and in the upper part of the underlying horizon (at depths of 80–185 cm; Figs 5, and 6). Grain-size data suggest that the accumulation of elements in this profile interval is related to the increase in physical clay content and the deposition of mud particles.

High and very high positive correlations were observed in the distributions of Bi, Cd, Ce, Cr, Ga, La, Mg, Na, Nd, Ni, Pb, Pr, Rb, Sm, Th, U, V, Y, Zn, and As. The distributions of these elements along the profile demonstrated moderate and high positive correlations with Co. They also showed moderate and sub-moderate correlations with Li (a high correlation was observed between Li and Mg) and a weak correlation with Ba. Finally, these elements exhibit a moderate negative correlation with Sr.

The coefficients of radial differentiation (R) were calculated for the studied soil. According to the average values of R , the studied section is characterised by intensive accumulation ($R > 5$) of the following elements in the soil profile compared to the parent rock: $Pb > As > Cd > Bi$. Moderate accumulation ($R = 2 - 5$) was characteristic of Sm, Cu, Li, Ni, Rb, and Ba. The order of weak accumulations ($R = 1 - 2$) was found to be: $Zn > Al > Gr > K > Ga > Mn > Mg > Ce > P > Th > Y > Na > Co > Pr > Nd > U > Fe > La > Sr$. Calcium was the only element that was removed from the soil ($R < 1$).

According to Dobrovolsky (Dobrovolsky, 1983) the Sr/Ba ratio indicates the hydrothermal conditions of sedimentation, which was confirmed by studies in Western Siberia, wherein the Sr/Ba ratio in sediments was closely related to climate humidification (Syso, 2004). Changes in the geochemical index of the palaeoclimatic Sr/Ba ratios (Fig. 5) are caused by fluctuations in the palaeoclimatic conditions. For the Late Holocene horizons, which are actively involved in the process of soil formation (up to a depth of 70 cm), the Sr/Ba values vary between 0.7–0.8, indicating that moisture conditions are close to those in modern climatic conditions. For the Late Holocene deposits located below 70 cm, the Sr/Ba value is 0.3–0.6, and represents a more humid climate than the modern one. In the Mid-Holocene sediments, this trend persists, and the indicator values range from 0.3 to 0.7. Based on the palaeomarker values between 0.7–0.9, an increase in climate aridisation was observed in the Early Holocene. In the Late Pleistocene sediments, which formed

closer to the Holocene boundary, the Sr/Ba ratio varies between 0.5–0.6, and indicates a period of increased moisture. For the underlying horizons of the Late Pleistocene, the palaeomarker values increase (0.8–0.9), and indicate a period of aridisation.

Co, Cu, Cr, and Zn can be indicators of warming/cooling climate; during cold periods, in the presence of a seasonally thawed layer, Cu, Co, Cr, and Zn are removed more intensively. A decrease in the coefficient values marks represents cooling, and vice versa, which is also observed for the territory of Eastern Siberia (Ivanova, 2019). For the Late Holocene horizons, which are actively involved in the soil formation process (up to a depth of 70 cm), the indicator values were lower relative to the entire section (except for Cu, which increased in this case because of its accumulation in the organo-mineral complexes); this indicated close to modern temperature conditions. For the Late Holocene sediments located below 70 cm, the indicator values are the highest, and indicate warmer conditions of sediment formation compared with modern sediments; this trend persists in the sediments of the Mid-Holocene. Based on the reduced values of Cu, Co, Cr, and Zn, climate cooling was inferred in the Early Holocene. In the Late Pleistocene sediments, whose formation was closer to the Holocene boundary, the value of these indicators increased, which indicates slight warming; for the underlying (more ancient) horizons of the Late Pleistocene, the indicator values subsequently became low and corresponded to cooling.

Among the studied elements, Al is especially remarkable: its highest content was reported in the upper Late Holocene horizon (15–20 cm depth), where it accumulated in organo-mineral complexes. Elements such as Cu and K were distinctly distributed uniformly along the entire profile, with an abrupt decrease in their contents in the lowermost 30 cm (Pleistocene), owing to their removal from sands. Iron distribution is relatively homogeneous along the profile; however, a considerable amount is observed in the upper Late Holocene horizon (10–20 cm depth), contrary to its removal in the Mid-Holocene horizon (155–160 cm depth). Morphological studies show that the level of the Mid-Early Holocene transition (200 cm depth) represents the formation of the geochemical barrier, wherein Fe^{2+} transitions to Fe^{3+} , and begins to precipitate. Manganese also shows a relatively uniform distribution with insignificant variations down to the Late Pleistocene-Early Holocene transition level (240–245 cm depth), wherein a clear geochemical barrier was noticed, below which this element was removed from the profile.

Phosphorus is highly abundant in the upper Late Holocene part of the profile owing to biogenic accumulation from plant and animal remains, with the respective enrichment of the humus horizon in this element.

The highest values of Ca content were reported in the 140–270 cm depth interval in the Late Pleistocene-Mid-Holocene horizons, which can be attributed to both the presence of mollusc shells in this interval (Makarchuk, 2019) and the formation of a geochemical barrier.

5. Discussion

The Berezovka-1 (IV) section was formed as a result of continuous sedimentation and had rather adequate chronological framework (Table 1).

The section began to form during the Late Pleistocene (21352–20314 cal yr BP). The lowest dated layer is located at a depth of 2.65–2.7 m, and is a light brown heavy

clay loam sample with traces of gleying. Its lower boundary coincides with the boundary of carbonate detection (effervescence occurs from 10-% HCL). Sediments at a depth of 2.45–2.5 m have an age of 13758–12930 cal yr BP, which corresponds to a subsequent stage of the Pleistocene. Deposits of this age have similar properties as described previously.

Higher in the section, at a depth of 2.05–2.1 m, the sediments are 9005–8605 cal yr BP, and belong to the Early Holocene (Walker et al., 2012); the sediments change to a darker heavy clay loam, where traces of gleying are weaker. The content of TOC was higher (3.4 %) compared to the surrounding layers, which may be due to the proximity of the optimum Mid-Holocene boundary.

Notably, the layer at a depth of 1.45–1.5 m was formed in the Mid-Holocene (5477–4985 cal yr BP). Sediments of this age are classified as heavy clay loam with increased carbonate contents (2.3 %), which appears as a whitish carbonate coating against a general brown background.

The horizon at a depth of 0.85–0.9 m is dated to 1241–803 cal yr BP (the Late Holocene). The sediments are classified as light clay with a high content of silty, and mud fractions. The horizon is distinguished by the lowest carbonate content along the profile, which may be due to increased humidity during this period of deposit formation relative to modern conditions. In the horizons of this age, the influence of modern soil-forming processes is also great, namely, the penetration of soil solutions from the surface and the high content of TOC (humus).

At a depth of 0.65–0.7 m and at the border of the darkest layer, sediments of the Late Holocene were formed at 291–151 cal yr BP. The sediments correspond to modern conditions of formation; the processes of soil formation are the most active at this depth, and the highest TOC content and an increased carbonate content are observed. This horizon has a lighter grain size composition (middle clay loam), and the large silt fraction is dominant.

The calculated Cc demonstrated the differences in the content of elements in the studied section compared to that in the global background. The Cc values for the elements U, Pr, Bi, Cd, and As are high and extremely high; the probable explanation for this is anthropogenic impact.

Based on the R values, we assumed that most of the elements were introduced during floods and high waters. During the Mid-Holocene and the beginning of the Late Holocene high water rises occurred in the Yenisey and Berezovka Rivers and thin mud material and chemical elements were introduced. These materials and elements were mainly derived from the destruction of mafic rocks and anthropogenic activities. This explains the high content of many (non-biogenic) elements (Bi, Cd, Mg, Na, Ni, Pb, Rb, Sm, U, V, Y, Zn, As et al.) in the middle of the section being of Late-Mid Holocene age and the clayey grain-size composition.

The flow of the Yenisey River was regulated in connection with the construction of the Krasnoyarsk hydroelectric power station about 50 years ago. The powerful floods and high water levels stopped and the influence of the river on sedimentation noticeably weakened in the tributaries of the Yenisey River, including the Berezovka River; this was reflected by the change in hydromigration processes and the strengthening of the influence of modern soil formation processes. Based on the morphological and grain-size studies of the section, we identified that the dynamics of the chemical element distribution depended on determined by the features of sedimentation. The same regularity of sedimentation from the Early Holocene to Late Holocene, showing progressive cooling and an increase

in climate humidity, was revealed by Yamskikh (Yamskikh, 2000) on the left bank of the Middle Yenisey valley (in the valleys of the Bobrovka, and Yazayevka rivers).

Based on the analysis of the Sr/Ba palaeomarker, and Cu, Co, Cr, and Zn indicators in the valley of the Berezovka River, we revealed that the periods in the Late Pleistocene changed from dry and cold (21 352–20 314 cal yr BP) to humid and warm (13 758–12 930 cal yr BP). During the Early Holocene (9005–8605 cal yr BP), the climate was more arid and colder. In the Late Holocene (1241–803 cal yr BP) and Mid-Holocene (5477–4985 cal yr BP), we observed an increase in humidification and climate warming compared to modern times. The climate was similar from the Late Holocene (291–151 cal yr BP) to modern times. This trend is confirmed by earlier palynological, lithological and paleohydrological studies conducted by A. F. Yamskikh and G. Yu. Yamskikh a comprehensive study of deposits in the 35–40 m terrace of the Yenisey River in the territory of the Krasnoyarsk depression (Yamskikh, 1987).

6. Conclusions

On the basis of our study, the following conclusions have been drawn.

The first floodplain terrace sediments in the valley of the Berezovka River began to form 20833 ± 519 cal yr BP (Late Pleistocene). The process of precipitation accumulation of the first floodplain terrace ended with the formation of the well-developed hydrometamorphosed alluvial dark humus soil.

Macromorphological studies revealed well-developed humification, and humus accumulation, as well as weak gleisation during formation of the terrace sediments. The grain size composition of the section ranged from light clay loam to light clay. The highest mud fraction content was reported in the middle of the sediments profile (69–137 cm depth), which is associated with the formation of clay minerals and the accumulation of most elements.

Based on geochemical analyses, the major elements in the studied section (at concentrations $>$ or $< 1 \cdot 10^{-2}$ %) were Al, Fe, Ca, Mg, K, Na, P, Mn, Rb, Ba, V, U, Sr, and Pr; the trace elements were Zn, Cr, Nd, Co, Ni, Ce, Ga, Li, La, Cu, Th, Pb, Y, As, Sm, Bi, and Cd. The content of certain elements exceed crustal Clarke values. U, Pr, Rb, V, Bi, Cd, As, Th, Ga, Co, Sm are showing such values. The order of elements with increasing Clarke values is as follows: $Sm < Th < Ga < Co < V < Rb < Pr < As < Cd < U < Bi$.

The fact that the contents of most elements are higher than crustal Clarke values is explained by the composition of the underlying and host rocks, which is also supported by mineralogical studies. However, the extremely high Clarke values of some elements indicate anthropogenic influence. The problem about extremely high bismuth content in the section remains debatable and requires further detailed research.

The distribution of most elements and their accumulation in the Mid-Late Holocene horizon (from 5477–4985 to 1241–803 cal yr BP) is explained by the high content of mud and clay minerals, which are good sorbents. Biogeochemical barriers were identified in the upper part of the section (accumulation of Al and P in organo-mineral complexes) and at a depth of 140–270 cm, representing the Late Holocene to the Mid-Holocene period (accumulation of Ca due to the presence of mollusc shells). Based on the R values, we assumed that most elements were introduced during floods and high waters. The abundance of feldspars, hornblendes, and pyroxenes, along with high amounts of Ti- and

Fe-containing minerals, indicates that sediments in the Berezovka River valley were disintegration products of mafic rocks.

The results of the geochemical characteristics of the sediments form the basis for comparing spontaneous and anthropogenic changes in the natural environmental in the Krasnoyarsk forest-steppe territory.

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Геохимия голоцен-позднеплейстоценовых отложений в долине р. Березовка (Приенисейская Сибирь)*

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Несмотря на огромную значимость, голоцен-поздне-плейстоценовые отложения слабо изучены в долинах рек на территории Красноярской лесостепи. В статье приведены детальные исследования геохимического состава отложений первой надпойменной террасы в долине р. Березовки, непрерывное накопление которых происходило в позднеплейстоцен-голоценовое время (начиная с 20833 ± 519 кал. лет назад), что имеет фундаментальное значение и является основой для дальнейших исследований природной среды при антропогенном влиянии в условиях Красноярской агломерации. Отложения перекрыты современной аллювиальной темногумусовой гидрометаморфизованной почвой. Макроморфологические исследования и исследование содержания гумуса выявили наличие хорошо развитых процессов гумусообразования и гумусонакопления, глеевого процесса. Установлено превышение кларков земной коры для нескольких элементов (U, Pr, Rb, V, Bi, Cd, As, Th, Ga, Co, Sm). Распределение большинства элементов и их накопление в среднем-позднем голоцене (от 5477–4985 до 1241–803 кал. лет назад) в средней части профиля объясняется высоким содержанием ила и глинистых минералов. На основании расчетов коэффициентов радиальной миграции установлено, что большинство исследованных элементов накапливались во время паводков и половодий. Полученные новые данные геохимических исследований на территории Красноярской лесостепи будут основой для сравнения спонтанных и антропогенных изменений состояния природной среды. Значения палеомаркеров свидетельствуют об изменении климатических условий в позднем плейстоцене от сухих и холодных к более влажным и теплым; в голоцене — от аридных и холодных (в раннем голоцене) к современным.

Ключевые слова: геохимия отложений, радиоуглеродное датирование, голоцен, первая терраса р. Березовки, аллювиальные почвы, Красноярская лесостепь, бассейн р. Енисей.

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