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Biophysicochemical properties of the eroded southern chernozem (Trans-Ural Steppe, Russia) with emphasis on the ^{13}C NMR spectroscopy of humic acids

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Abstract: The morphological, water-physical and chemical properties, basal respiration of the southern chernozem (Chernozem Haplic Endosalic) and erosional sediment in the Trans-Ural steppe zone (Republic of Bashkortostan, Russia) were studied. The surface soil horizon significantly differs from the sediment by the better structure and water aggregate stability. The particle size distribution of the sediments, due to erosion, contains more silt and clay fractions compared to the slope soil. It indicates a great potential for the carbon saturation of the soil which is limited by degradation. The slope soil is slightly saline, the type of the salinisation is sulfate with the participation of hydrocarbonates. The CO_2 emissions, the organic carbon and alkaline-hydrolysable nitrogen content is low; and significantly lower than in the erosional sediment, but the content of exchangeable cations and water-soluble salts is higher. The structural composition of the humic acid (HA) extracted from the soil and erosional sediments was determined by ^{13}C NMR spectroscopy. Aliphatic structural fragments predominate (65%) with a maximum signal level in the area of C, H-alkyls in the HA of the surface horizon. In the HA of the erosional sediment, the proportion of aromatic structural fragments is higher (up to 59%), which is associated with the processes of hydrolysis and condensation. In the HA of the slope soil, the formation of predominantly C, H-alkyls, oxygen-containing groups, including carboxyl ones, takes place. Differences in the composition of the structural fragments and functional groups of the soil and sediment HA are due to the different stability of the organic matter under conditions of the development of the soil erosion processes.

Keywords: carbon sequestration; erosion; nuclear magnetic resonance; sediment; soil properties

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Soil organic carbon (SOC) is a crucial element in the global environmental carbon cycle (Schimel 1995; Dutta et al. 2006). SOC plays a key soil function as it is important for stabilising the soil structure, and retaining/releasing nutrients for plants. The SOC loss negatively affects the availability of the soil nutrients and also affects the climate change (Semenov et al. 2013). The chernozem zone is a "hot spot" in terms of the SOC content; additionally, the environmental changes in this zone could have an impact on the climate change (Höfle et al. 2013; Lefèvre et al. 2017). SOC is released into the atmosphere via greenhouse gases, especially CO_2, and other emissions (Knoblauch et al. 2013).

The intensive and long-term use of chernozem soils in the former Soviet Union led to a decrease in their fertility (Gabbasova et al. 2016; Golosov et al. 2022). Moreover, due to improper land management, the amount of eroded areas increased. Nowadays the situation is also exacerbated due to climate change, which is manifested by decreasing the precipitation and increasing the air temperatures in arid and semi-arid zones. Such regions become more vulnerable to droughts, the development of erosion and salinisation processes, and increase the risks of desertification as a whole (Kattsov 2017). The Trans-Ural region of the Republic of Bashkortostan (RB) belongs to such a region and the above-mentioned negative processes are also observed in this steppe zone (Sobol et al. 2015). Moreover, most of the saline soils in the RB area are located there and about 55% of the agricultural land is subjected by erosion processes (Gabbasova et al. 2016); whose rates could increase due to climate change and anthropogenic impacts. Such ongoing conditions are conducive to decreasing the soil fertility even further. Nevertheless, with soil conservation practices (e.g., for erosion control – crop rotation, reduced tillage, mulching, cover cropping, cross-slope farming; for salinisation control – using salt-free organic fertilisers, soil salt reducing by leaching irrigation and phytoextraction by plants), it is possible to restore and improve the soil health, which will also increase the carbon saturation of steppe soils (Wiesmeier et al. 2018). Thus, studying the SOC by precise methods becomes relevant, especially in semi-arid zones (Nicolás et al. 2012).

Various spectral methods are used to study the SOC (Yao et al. 2019), the main of which are: nuclear magnetic resonance (NMR) spectroscopy, electron paramagnetic resonance, infrared spectroscopy, and densitometric fractionation (Thompson & Chersters 1970; Cocozza et al. 2003; Ovsepyan et al. 2020). NMR spectroscopy is a highly accurate tool for studying the qualitative and quantitative characteristics of organic matter (Ejarque & Abakumov 2016; Chukov et al. 2018). The advantage of the ^{13}C NMR method is the ability to quantify the content of the structural fragment groups and to identify the individual structural fragments in humic substances (HS), in particular, in humic acid (HA) molecules. HS are group of dark-coloured substances that have similar structural features, but are not individual agents. Their composition and properties are determined by local formation conditions (climate, precursors of humification, composition and activity of the soil microbiota) (Orlov 1995; Piccolo 1996). HS have a whole complex of mechanisms influencing the state of the soils, plants, and soil microbiome. In terms of ecosystem services, the HS in the soils is involved in the regulation of the atmosphere (Polyakov & Abakumov 2021). This is associated with the formation of compounds in the HA that are stable to biotic and abiotic influences. Nowadays, the actual research of HS is related to the study of the impact of HA on arable land and in land management, and they can also be used to prevent the spread of oil spills, soil erosion, and to reduce the pollution of water bodies from mineral fertilisers introduced into the soil (Banach-Szott et al. 2021). Thus, HS have become most widespread in the field of point farming, since the application of various humates has a positive effect on the growth of agricultural production, the redistribution of nutrients and their availability to plants (mobilisation).

The aim of this research is to identify the differences in the southern chernozem and its erosion deposits in the Trans-Ural region. The specific topics: (*i*) study the morphological, chemical and physical properties of the soil and sediments; (*ii*) evaluate the chemical and structural composition of HS using ^{13}C NMR spectroscopy; (*iii*) and estimate the SOC storage potential.

MATERIAL AND METHODS

Study area and soil sampling description. This study was carried out in the steppe zone of Trans-Ural region (Khaibulinsky district, RB, Russia) (Figure 1). A typical slope with a pronounced development of erosion processes and a small dry valley were chosen as the objects of the research. The studied

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area is a 3-year fallow field (previously – long-term cultivated/ploughed). The soil is an eroded southern chernozem (Chernozem Haplic Endosalic according to the World Reference Base (WRB) (IUSS Working group WRB 2015)), characterised by a lightly solonetzic, thin humus-accumulative (A+AB) horizon with a low SOC content. In the region, southern and ordinary chernozems predominantly occur (Chernozem Calcic (IUSS Working group WRB 2015)) with varying degrees of salinity and alkalinity (Khaziev et al. 1995). They are formed on diluvial yellow-brown carbonate clays and heavy loams, often containing large amounts of water-soluble salts. The underground water is mostly highly mineralised by a bicarbonate-sulfate or sodium chloride composition and located at a low depth (10–25 m) (Abdrakhmanov & Popov 1999).

The climate in the study area is moderately warm and arid (Dfb according to the Köppen–Geiger climate classification). The average annual air temperature is 1.8 °C (about +19 °C in July, –17 °C in January) with 308 mm of precipitation. The relief is a foothill-plain and ridge-hilly with altitudes of 270–450 m. The vegetation is mainly represented by *Festuca valesiaca* and *Stipa pennata*.

Five soil pits were excavated until the parent material on studied slope was reached, the samples were taken from each genetic horizon: A_1 (0–12 cm), AB (12–37 cm) and B (37–53 cm), and five surface sediments were collected from the accumulation zone in the dry valley (Figure 1). The samples were prepared in a standard way (dried, sieved, etc.) and were used for the subsequent laboratory analyses. The results were averaged and presented in tables/pictures with the error of measurement (± SEM).

Chemico-biological analyses were conducted by standard procedures (Arinushkina 1970). In particular, the SOC content was determined by the Tyurin titrimetric (wet combustion) method in Nikitin's modification with spectrophotometric termination according to Orlov and Grindel (Orlov & Grindel 1967). The gradation of the SOC on the categories was carried out according to the scale (Semenov & Kogun 2015), where the content > 5.8% is characterised as very high, 3.5–5.8 is characterised as high, 2.3–3.5 is characterised as average, 1.4–2.3 is characterised as low and < 1.4 is characterised as very low. Alkaline hydrolysable nitrogen was extracted at 1 mol/L KCl (1 : 2.5 soil/solution) according to the Cornfield method; the available phosphorus and exchangeable potassium were extracted at 0.5 mol/L CH_3COOH at a 1 : 2.5 soil/solution ratio by the Chirikov method; the exchange cations Ca^{2+} and Mg^{2+} were determined by the trilonometric method; soil reaction – poten-

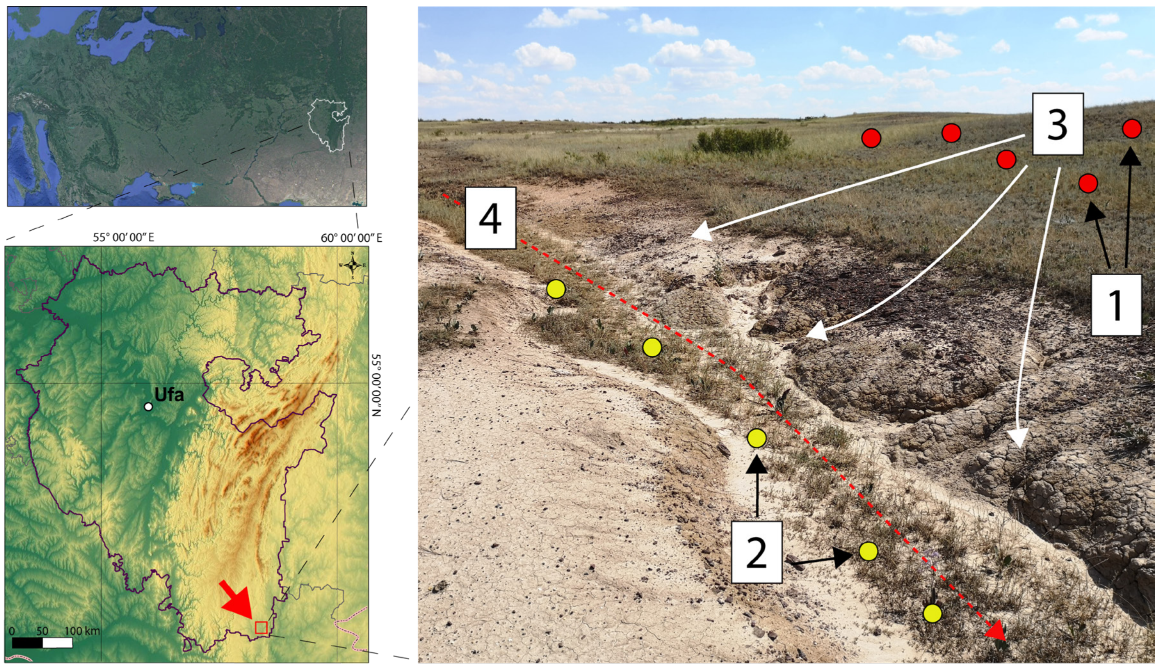

Figure 1. Location of the study area, soil sampling points and directions of the erosional runoff
1 (red circles) – Chernozem Haplic Endosalic; 2 (yellow circles) – erosion deposits; 3 – direction of the surface runoff and soil washout; 4 – direction of the main temporary water flows

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tiometry (at 1 mol/L KCl suspension (1 : 2.5 soil/solution)). The water-soluble salts were measured in 1 : 5 (soil to water) extractions. The degree of soil salinity was assessed according to the dry residue content (%), where: < 0.25 characterises non-saline soils, 0.25–0.5 characterises slightly saline, 0.5–1 characterises medium, 1–2 characterises high, and > 2 characterises extremely saline (Mamontov 2002). The microbiological activity of the soils (basal respiration) was determined using an incubation chamber by using the Jenkinson and Powlson (1976) method.

The soil structure and texture measurements were performed according to the methodology of Vadyunina and Korchagina (1986). In particular, the structural-aggregate composition (dry sieving) was determined by using meshes with sizes of 10, 7, 5, 3, 1, 0.5 and 0.25 mm. The soil aggregate stability (wet sieving) was measured using a Baksheev device (Vibrotehnic, Russia); the particle size distribution was measured by a Laska-TD laser diffraction analyser (Biomedical Systems, Russia).

The gradation of water-physical properties of the soil/sediments on the categories are made according to the Russian classification (Vadyunina & Korchagina 1986). The soil aggregate stability was classified as follows: < 30% – unsatisfactory, 30–40 – satisfactory; 40–75 – good and > 75 – excessively high. The coefficient of the soil structure (Cst), where a value > 1.5 is classified as excellent, 1.5–0.67 is classified as good and > 0.67 is classified as unsatisfactory.

SOC saturation. The fine (clay and silt) fractions play a significant role in the mechanism of the SOC stabilisation/accumulation for mineral soils. Hassink (1997) revealed that the amount of SOC (for most temperate zone soils) is strongly correlated with the fine fraction content. Based on this approach, the SOC storage potential was determined according to the equation proposed by Six et al. (2002):

$$\text{Csat} = 16.33 + 0.32 \times \text{fine fraction } (< 0.05 \text{ mm})$$

where:
Csat – the SOC saturation (g/kg);
fine fraction – the content of the particle size < 0.05 mm (%).

Extraction of HA. Evaluating the chemical composition of HS using ^{13}C NMR spectroscopy was performed for the topsoil (humus horizon A_1) and the erosional sediment. For the isolation of the HA from the soil, the standard International Humic Substance Society (IHSS) method was used (Swift 1996). The initial soil samples, sieved through a 1 mm sieve, were decalcified in a solution of 0.05N H_2SO_4 for one day. Then, after filtration, the decalcified solution was poured out, and a soil-solution of 0.1N NaOH was poured into the sample with soil in a ratio of 1 : 10 and left for one day. After that, the supernatant was decanted and a coagulant (saturated solution of Na_2SO_4) was added. The next day, the solution was filtered again. To precipitate the HA from the solution, a 1N H_2SO_4 solution in a ratio of 50 mL of acid/100 mL of supernatant was used and left for a day. The HA gel was collected in plastic (dialysis) bags and placed in distillate water for 7 days. The water in the distillate tanks was changed every day. After dialysis, the gel was placed on Petri dishes and dried at room temperature.

^{13}C NMR spectroscopy. The solid-state spectra of the HA were determined by CP/MAS ^{13}C-NMR spectroscopy on a Bruker Avance 500 NMR spectrometer (Bruker Corporations, USA) in a 3.2 mm ZrO_2 rotor (Bruker Corporations). The magic-angle rotation speed was 20 kHz, and the nutation frequency for the cross-polarisation of u1/2p 1/4 was 62.5 kHz. The repetition delay was 3 s. Number of scans performed was 18 432 at 21 °C. The chemical shifts were calculated from the absolute values in the MestreNova software (Ver. 12.0.0-20080, 2017). The obtained signals were from the non-polar alkyls (0–46 ppm), N-alkyl/methoxyl (46–60 ppm), O-alkyl and anomers (60–110 ppm), aromatics (110 to 160 ppm), and carboxyl, esters, amides (160–185 ppm). The quinone group (185–200 ppm) was not found. The sums of the signals in the studied spectra were determined using MestreNova (Ver. 12.0.0-20080) software. To construct a diagram of the integral indicators of the HA's molecular composition, the following indices were used – the degree of hydrophobicity and the degree of humification. The degree of hydrophobicity (aliphatic fragments (AL) h,r + aromatic fragments (AR) h,r is the total fraction of the unoxidised carbon atoms, i.e., substituted with the hydrogen atoms or other AL and calculated as the sum of signals from the C,H-alkyls and OCH groups. The C,H–AL/O,N–AL parameter is the degree of decomposition of the organic matter (humification), calculated as the ratio of the signals in the region of the C,H-Alkyls to the sum of the signals from the OCH group (OCH/OCq) and O,N-Alkyls.

RESULTS AND DISCUSSION

Morphological properties. For a more detailed characterisation of the studied soil and erosion sediment, their descriptions are given below (Table 1).

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Table 1. Description of the slope soil and erosion sediment

Soil genetic horizon (depth, SEM ± 4 cm)	Morphological properties
Chernozem Haplic Endosalic (coordinates: E 51.84316 N 58.38052; SEM ± 5 m)	
A_1 (0–12)	Eroded slope. Fine gravel on soil surface. Light grey with a brownish tint, dry, crumbly medium-grained, sandy loam (soil texture was determined by feel), low compacted, rarely any roots and small pebbles, smooth transition in colour.
AB (12–37)	Heterogeneously coloured with transverse stripes (up to 5 cm) in light grey, brownish and burgundy shades, moist, granular-lumpy, loam, medium compacted, the transition is sharp in colour.
B (37–53)	Brown with a burgundy tint, wet, crumbly nut-shaped, clay loam, high compacted, large whitish calcareous inclusions.
Erosion sediment (coordinates: E 51.84341, N 58.38052 SEM ± 5 m)	
0–7	Light grey, dry, unstructured, loam, medium compacted. Ferruginous rubble on the surface.

SEM – standard error of the mean

According to the field morphological characteristics (Krasilnikov et al. 2009), the soil corresponds to southern chernozem (Chernozem Haplic Endosalic). Khaziev et al. (1995) noted: (*i*) within the Trans-Ural region, such soils are located in the southeast, predominantly in the Khaibulinsky district; (*ii*) Chernozem Haplic Endosalic is characterised by a thin humus-accumulative horizon (~ 43 cm), slightly effervescence with 10% HCl of a topsoil layer, with a strong illuvial horizon (B) and the parent material (C) enriched by carbonates; (*iii*) The soil profile has dark grey streaks in the form of tongues from the overlying (A and AB) horizons. During period droughts, strong desiccation causes the formation of deep cracks, which are filled with fine earth. Cracks also occur in severe winters with little snow, when the soils freeze deeply. All this information corresponded to the soil that we studied.

Water-physical properties. The structural and aggregate state of the southern chernozem is characterised as good. Throughout the soil profile, the amount of agronomically valuable aggregates (Σ 0.25–10 mm; Vadyunina & Korchagina 1986) was higher than 60% (84.0–97.2%), and the Cst exceeded 1.5 (Table 2). Down the profile, a deterioration in the soil structure was noted, this is due to an increase in the proportion of the silt fractions and a slight decrease in the soil water resistance. The soil aggregate stability in horizons A_1 and AB is characterised as excessively high, and is characterised as excellent for B. In general, the main parameters of the soil profile correspond to southern chernozems and are consistent with

Table 2. The structural and aggregate composition of the soil and sediments

Horizon (depth, cm); sieving type		Particle content (%) > 10 (mm)	10–7	7–5	5–3	3–1	1–0.5	0.5–0.25	< 0.25	Cst	Soil aggregate stability (%)
Chernozem Haplic Endosalic											
A_1 (0–12)	D	9.9 ± 0.3	3.9 ± 0.1	4.0 ± 0.1	11.2 ± 0.5	17.6 ± 0.6	35.4 ± 1.1	14.3 ± 0.4	3.7 ± 0.1	6.4 ± 0.2	90.8 ± 3.4
	W	–	15.0 ± 0.6	5.8 ± 0.2	8.2 ± 0.3	27.9 ± 0.9	22.3 ± 0.8	11.6 ± 0.3	9.2 ± 0.4		
AB (12–37)	D	4.2 ± 0.1	3.1 ± 0.1	4.4 ± 0.1	24.4 ± 1.0	31.7 ± 1.2	16.2 ± 0.6	5.7 ± 0.2	10.3 ± 0.4	5.9 ± 0.2	89.3 ± 4.0
	W	–	5.4 ± 0.3	6.1 ± 0.2	31.6 ± 1.1	17.7 ± 0.5	3.1 ± 0.1	26.4 ± 0.9	10.7 ± 0.4		
B (37–53)	D	1.4 ± 0.1	0.8 ± 0.1	1.6 ± 0.1	20.5 ± 0.8	57.4 ± 1.8	16.4 ± 0.5	0.5 ± 0.1	10.4 ± 0.3	3.5 ± 0.1	62.5 ± 2.1
	W	–	1.4 ± 0.1	2.7 ± 0.1	30.6 ± 1.2	11.5 ± 0.3	2.0 ± 0.1	14.3 ± 0.5	37.5 ± 1.5		
Erosion sediments											
0–7	D	7.0 ± 0.3	10.7 ± 0.4	10.1 ± 0.4	17.6 ± 0.7	18.0 ± 0.6	17.6 ± 0.6	10.0 ± 0.4	9.0 ± 0.3	5.2 ± 0.2	39.9 ± 1.7
	W	–	8.9 ± 0.3	5.7 ± 0.2	6.9 ± 0.3	7.6 ± 0.3	4.6 ± 0.1	6.2 ± 0.1	60.1 ± 1.9		

Cst – coefficient of the soil structure; D – dry; W – wet

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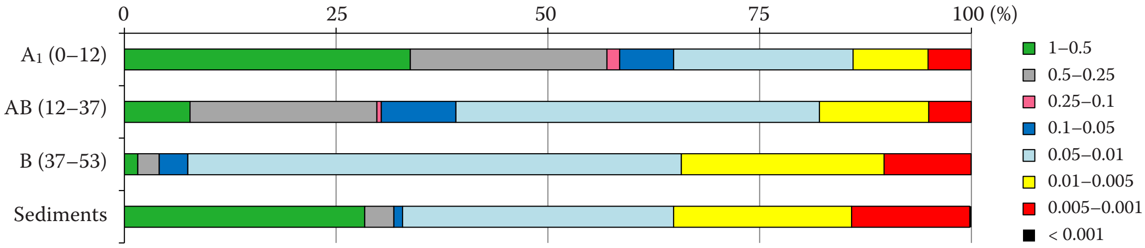

Figure 2. Particle size distribution of the Chernozem Haplic Endosalic and erosion sediments

the data of other researchers (Khaziev et al. 1995). For example, Khasanova et al. (2014), studying the physical properties of the chernozems in the Trans-Ural region, revealed that, depending on the land use type, the water resistance varies within 35–73%. The proportion of dusty fractions (structural aggregates < 0.25 mm) varied from 8.2 to 12.6%, while the lumpy fractions (> 10 mm) varied from 15.7 to 24.0%.

The structure of the sediments is assessed as good, the aggregates stability is satisfactory. The weak resistance of the deposited aggregates to destruction by water, on the one hand, is associated with the nature of their origin. In particular, the sediments consist of loosely coupled fine particles from the already washed out/blown particles from the slope. On the other hand, the weak water resistance of the erosion material is due to the low SOC and nutrient contents. A violation of the balance of humic compounds and some cations in the soil reduces the process of structure formation of water-stable aggregates. According to Tsybulko et al. (2005), water-stable aggregates of small sizes are formed in the soil with a low SOC content (less than 2%), and aggregates larger than 3 mm are formed in the soil with a high SOC.

The granulometric composition of the humus-accumulative horizons (A and AB) of the southern chernozem is characterised as sandy loam; the illuvial horizon is loam, with a dominance of very fine sand fractions (~58%) (Figure 2). The texture of the erosion material is loam. The high content of physical clay (<0.01 mm) (~65%) in the sediments is undoubtedly associated with the development of erosion processes on the slope. Thus, in the upper soil layer of the slope, the proportion of physical sand (> 0.01 mm) was 86%, which is 21% higher than that in the sediments. This indicates the washing/blowing out from of the fine-dispersed fraction the slope soil and their deposition in places of depression in the hydrographic network, in particular in gullies, micro-ravines, furrows of temporary watercourses, etc. For example, during the development of water erosion on leached chernozems in the Cis-Ural region, silt and clay fractions predominate in the composition of suspended/deposited sediments, in both cases: after snowmelt (Komissarov & Gabbasova 2014) and rainfalls (Komissarov & Gabbasova 2017).

Chemical properties. The chernozem profile is characterised by a "low" SOC content in the humus horizon (A_1) and very low in the underlying layers (Table 3). The pH belongs to the slightly alkaline category, with negligible increasing values with the depth. The cation exchange capacity in the upper horizon is the lowest (26.3 cmol(eq)/kg), increasing twice with the depth (53.9 cmol(eq)/kg). Calcium is dominated by the absorbed cations throughout the

Table 3. Chemical properties of the soil and sediments

Horizon (depth, cm)	pH (H_2O)	SOC (%)	Ca^{2+}	Mg^{+2}	Na^{+}	Alkaline hydrolyzable nitrogen, (mg/kg)	Basal respiration (mg CO_2/g)
			(cmol(eq)/kg)				
Chernozem Haplic Endosalic							
A_1 (0–12)	7.68 ± 0.25	1.77 ± 0.06	18 ± 0.6	8 ± 0.3	0.3 ± 0.01	112 ± 4	31.4 ± 1.1
AB (12–37)	7.65 ± 0.32	1.05 ± 0.04	27 ± 1.1	16 ± 0.7	1.2 ± 0.04	56 ± 2	nd
B (37–53)	7.88 ± 0.29	1.02 ± 0.04	33 ± 1.3	20 ± 0.7	0.9 ± 0.03	14 ± 1	nd
Erosion sediments							
0–7	7.58 ± 0.31	1.09 ± 0.03	38 ± 1.3	10 ± 0.4	0.8 ± 0.03	56 ± 2	18.8 ± 0.9

SOC – soil organic carbon; nd – no data

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Table 4. Data of the water extracts from the soil and sediments

Horizon (depth, cm)	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	Dry residue (%)
	(cmol(eq)/kg)							
Chernozem Haplic Endosalic								
A_1 (0–12)	0.08 ± 0.003	0.96 ± 0.035	0.06 ± 0.002	4.81 ± 0.159	1.65 ± 0.072	2.95 ± 0.091	1.31 ± 0.051	0.34 ± 0.014
AB (12–37)	0.04 ± 0.001	0.76 ± 0.031	0.13 ± 0.005	14.80 ± 0.537	3.91 ± 0.173	7.08 ± 0.276	5.73 ± 0.195	1.05 ± 0.039
B (37–53)	0.08 ± 0.002	0.88 ± 0.029	0.10 ± 0.004	19.58 ± 0.675	9.20 ± 0.352	9.61 ± 0.317	3.86 ± 0.152	1.49 ± 0.048
Erosion sediment								
0–7	0.04 ± 0.001	0.16 ± 0.006	0.19 ± 0.007	11.60 ± 0.398	3.82 ± 0.143	4.78 ± 0.205	3.39 ± 0.142	0.81 ± 0.031

soil profile, but the proportion of magnesium is also quite high, especially in the illuvial horizon. The presence of exchangeable sodium from 1.2 to 2.8% of the sum of the cations defines the solonetzisation of the chernozem. It is interesting to note that the composition of cations in the sediments is noticeably different from the slope soil, and has the highest (78%) calcium and low (20%) magnesium content. The proportion of sodium (as well its total content of cations) is higher than in the topsoil. The content of alkaline-hydrolysable nitrogen in the soil is moderate and decreases sharply with the depth. The content of nitrogen, SOC and pH of the erosion material is very close to the values of the AB horizon. The sediments contained half of such values than in the slope humus horizon. Similar results for the microbiological activity in the sediments were observed in the Trans-Ural region for the foothill soils (Chernozems Haplic) (Suleymanov et al. 2021). It was found that the basal respiration was 12.6 mg CO_2/g in the sediments, with an average 18.8 mg CO_2/g in the eroded slope, and 30.1 mg CO_2/g in the non-eroded plots characterised by a high SOC content.

The studied soil profile is saline (Table 4). The humus horizon is slightly saline, while the transitional (AB) and illuvial (B) horizons are highly saline. The salinity type is sulfate with participation of hydrocarbonates. The erosion sediment is characterised by a medium degree of sulfate type salinisation.

Carbon saturation. The topsoil has the potential for carbon saturation up to 27.6 g/kg (for the case of the fine fraction proportion – 35.2%). In other words, this horizon (A_1) can accumulate an additional (the maximum capacity) 35.9% (9.9 g/kg) of the SOC. However, such results can be achieved without the development of degradation processes. Since, as mentioned before, the active detachment of fine particles occurs due to runoff/erosion. Moreover, there is concern about climate change in the region. Sobol et al. (2015) identified the intensification of denudation and deflation processes in the study area, in particular, the average monthly maximum wind speeds (up to 45 m/s), the number of dust storms and the intensity of rare rains (precipitation erosion index R30) have increased.

^{13}C NMR spectroscopy of HA. The aliphatic structural fragments (ALSF) were predominant (65%) in the slope soil. The maximum signal level was recorded in the zone of the C,H-alkyls, which indicates the formation of a branched net of simple carbon bonds ($(CH_2)n/CH/C$ and CH_3). The character of the soil spectrum is comparable to the previously studied Chernozem Haplic in the European part of Russia (Trubetskoi & Trubetskaya 2011; Danchenko et al. 2020). The predominance (up to 59%) of the aromatic structural fragments (ARSF) was noted in the sediments. Figure 3 shows the spectra of the HA. The presence of signals in the same groups of structural fragments indicates the identity of the humification precursors in the study area.

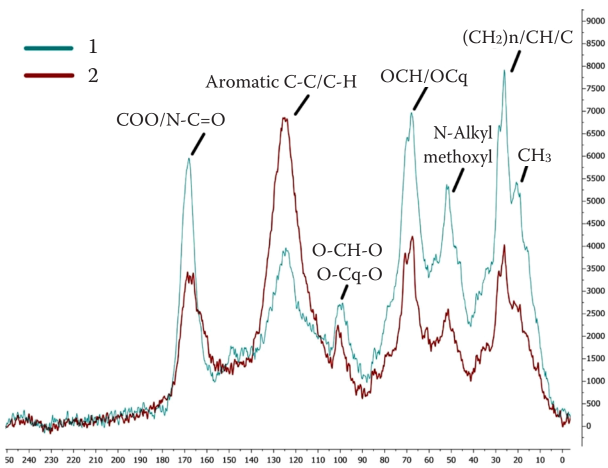

Figure 3. ^{13}C CP/MAS NMR spectroscopy of the humic acid extracted from the: 1 – chernozem (A_1 horizon), 2 – erosion sediment

X-axis – chemical shifts (ppm); *Y*-axis – intensity of the signal

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Table 5. The content of the structural fragments in the humic acid (HA)

	Chemical shifts in % from ^{13}C						AR	AL	AR/ AL	AL h,r+ AR h,r	C,H-AL/ O,N-AL
	0–46	46–60	60–110	110–160	160–185	185–200					
Chernozem Haplic Endosalic (A_1)	32	13	20	15	20	0	35	65	0.53	47	0.96
Erosion sediments	22	7	12	49	10	0	59	41	1.43	71	1.20

AR (aromatic fraction) – the sum of the AR structural fragments; AL (aliphatic fraction) – the sum of the AL structural fragments; AL h, r + AR h, r – degree of hydrophobicity (%); C,H-AL/O,N-AL – degree of humification

The higher level of the HA's aromaticity in the eroded material may be related to the hydrolysis process of the ALSF and the condensation of the ARSF. At the same time, a significant proportion of the ARSF (that are stable in the environment) are preserved and condensed. This is also confirmed by the microbiological activity: the basal respiration in the sediments at almost 2 times lower than in the A_1 horizon. Table 5 presents data on the calculation of the absolute signals according to the ^{13}C-NMR spectroscopy.

In the slope's topsoil, the formation of C,H-alkyls ($(CH_2)n/CH/C$ and CH_3), the oxygen-containing group OCH (OCH/OCq), and the carboxyl group (–COOR) predominantly occur. The vegetation cover in this area is represented by vascular plants, whose chemical composition, as known, are dominated by various carbohydrates (mono- and oligosaccharides, cellulose, etc.) with a small proportion of arenes (tannins, flavonoids and lignin). The sediments are rich in aromatic compounds of C-C/C-H, C,H-alkyls ($(CH_2)n/CH/C$ and CH_3, as well OCH (OCH/OCq). The study conducted by Suleymanov et al. (2021) in the Trans-Ural shows that, on foothills, the Chernozem Calcic (SOC content higher than in Chernozem Haplic) accumulated more ARSF in the sediments (HA AR/AL = 0.67) compared to eroded soil. It should be noted that the highest content of ARSF was in the non-eroded soil (20% more than in the sediment). Numerous studies have shown that long-term conventional ploughing leads to a decrease in the ALSF and an increase in the ARSF and the carboxylic groups in chernozems (Kholodov et al. 2011; Vishnyakova et al. 2011). Similar results were obtained for soils of the forest-steppe zone. In areas not affected by degradation, the predominant accumulation of ALSF (up to 64%) was detected. For example, under wildfire conditions, as a factor of the SOC degradation, a slight increase in the ARSF was observed (Abakumov et al. 2017). This may also indicate the selection of more stable organic compounds in the environment.

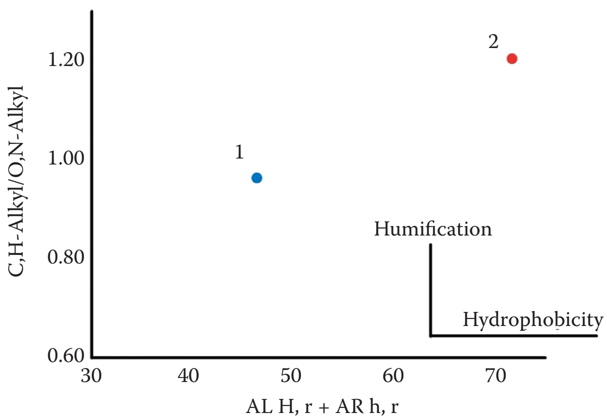

Figure 4. Diagram of the integral indicators of the humic acid's (HA) molecular composition in the: 1 – chernozem, 2 – erosion sediment

AL h, r + AR h, r (%) – degree of hydrophobicity; C,H-AL/O,N-AL – degree of humification

Compared with the slope soil, the erosion deposits were characterised by more humified SOC, with a relatively high degree of hydrophobicity (Figure 4). A similar result was obtained for Chernozem Calcic – the organic matter of the sediments was also characterised not only by an increased degree of the SOC's decomposition, but also by the hydrophobicity (Suleymanov et al. 2021).

Thus, in the areas of erosion sediment accumulation (small dry valleys), the SOC of the deposits is more resistant to biodegradation and its transformation is slow. The mineralisation processes, microbiological activity, availability of biogenic elements to plants and microorganisms are also lower than it in the slope soil.

CONCLUSION

The Chernozem Haplic Endosalic in the Trans-Ural steppe region is slightly saline, slightly eroded, with a low SOC content. The soil is characterised by a good (Cst = 6.35) structural-aggregate composition, ex-

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cessively high (91%) water resistance of aggregates in the upper layer. The structurisation of the erosive sediment is somewhat worse (Cst = 5.24), and the sum of the water-stable aggregates was only 40%, which corresponds to the satisfactory category. The particle size distribution of the slope soil and erosive material are different: the texture of the humus horizon is sandy loamy, and the erosive material is loam; the content of physical clay in deposits was 32% higher, which is associated with the development of the erosion processes (washout/blowing of fine fractions from the slope soil). The sediments are characterised by a significantly lower content of SOC and alkaline-hydrolysable nitrogen, as well CO_2 emissions. Nevertheless, the sediments contain higher exchangeable cations and water-soluble salts compared to the humus horizon.

ALSF predominate (65%) in the HA composition of the topsoil, with the maximum level of signals in the C,H-alkyl diapason. The proportion of ARSF (up to 59%) in the HA of the sediments is higher, which is associated with the hydrolysis and condensation processes. In the HA of the slope soil, the formation of the C, H-alkyls, oxygen-containing groups, including carboxyl ones, predominantly occur. Differences in the composition of the structural fragments and functional groups of the HA in the soil and sediment are due to the different stability of the SOC under the development of erosion processes. The SOC of the sediments is more resistant to biodegradation and its transformation processes are slower. The microbiological activity and greenhouse gas emissions in the erosion material are lower, when compared to the slope soil. A high potential for SOC sequestration for the humus horizon was revealed. However, such potential is very limited due to the changing climatic indicators that lead to the degradation processes (erosion and salinisation). Thus, the best management practices are needed to improve the soil's health and SOC sequestration potential, since the degradation of steppe soils in the Trans-Ural region leads to severe limitations for agricultural activities.

REFERENCES

Abakumov E., Maksimova E., Tsibart A. (2017): Assessment of postfire soils degradation dynamics: Stability and molecular composition of humic acids with use of spectroscopy methods. Land Degradation & Development, 29: 2092–2101.

Abdrakhmanov R.F., Popov V.G. (1999): Mineral Medicinal Waters of Bashkortostan. Ufa, Gilem. (in Russian)

Arinushkina E.V. (1970): A Handbook of Chemical Analysis of Soils. Moscow, Moscow State University. (in Russian)

Banach-Szott M., Debska B., Tobiasova E. (2021): Properties of humic acids depending on the land use in different parts of Slovakia. Environmental Science and Pollution Research, 28: 58068–58080.

Chukov S.N., Lodygin E.D., Abakumov E.V. (2018): Application of ^{13}C NMR spectroscopy to the study of soil organic matter: A review of publications. Eurasian Soil Science, 51: 889–900.

Cocozza C., D'orazio V., Miano T.M., Shotyk W. (2003): Characterization of solid and aqueous phases of a peat bog profile using molecular fluorescence spectroscopy, ESR and FT-IR, and comparison with physical properties. Organic Geochemistry, 34: 49–60.

Danchenko N.N., Artemyeva Z.S., Kolyagin Y.G., Kogut B.M. (2020): Features of the chemical structure of different organic matter pools in Haplic Chernozem of the Streletskaya steppe: ^{13}C MAS NMR study. Environmental Research, 191: 110205.

Dutta K., Schuur E.A.G., Neff J.C., Zimov S.A. (2006): Potential carbon release from permafrost soils of Northeastern Siberia. Global Change Biology, 12: 2336–2351.

Ejarque E., Abakumov E. (2016): Stability and biodegradability of organic matter from Arctic soils of Western Siberia: Insights from ^{13}C-NMR spectroscopy and elemental analysis. Solid Earth, 7: 153–165.

Gabbasova I.M., Suleimanov R.R., Komissarov M.A., Garipov T.T., Sidorova L.V., Khaziev F.K., Khabirov I.K., Fruehauf M., Liebelt P. (2016): Temporal changes of eroded soils depending on their agricultural use in the southern Cis-Ural region. Eurasian Soil Science, 49: 1204–1210.

Golosov V.N., Paramonova T., Kust G., Litvin L., Andreeva O. (2022): Identification of soil resources problems in European Russia. In: Li R., Napier T.L., El-Swaify S.A., Sabir M., Rienzi E. (eds.): Global Degradation of Soil and Water Resources. Singapore, Springer: 449–473.

Hassink J. (1997): The capacity of soils to preserve organic C and N by their association with clay and silt particles. Plant and Soil, 191: 77–87.

Höfle S., Rethemeyer J., Mueller C.W., John S. (2013): Organic matter composition and stabilization in a polygonal tundra soil of the Lena Delta. Biogeosciences, 10: 3145–3158.

IUSS Working Group WRB (2015): World Reference Base for Soil Resources 2014. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps (Update 2015). Rome, FAO.

Jenkinson D.S., Powlson D.S. (1976): The effects of biocidal treatments on metabolism in soil – V: A method for measuring soil biomass. Soil Biology and Biochemistry, 8: 209–213.

Kattsov V.M. (2017). Report on Climate Risks in the Russian Federation. Saint Petersburg, FGBU "GGO". (in Russian)

https://doi.org/10.17221/52/2022-SWR

Khasanova R.F., Suyundukova M.B., Suyundukov Ya.T., Akhmetov F.R. (2014): Optimization of agrophysical properties of ordinary chernozem under the influence of perennial grasses. Fundamental Research, 8–5: 1095–1099.

Khaziev F.K. (1995): Soils of Bashkortostan. Vol. 1. Ecologic-genetic and Agroproductive Characterization. Ufa, Gilem. (in Russian)

Kholodov V.A., Konstantinov A.I., Kudryavtsev A.V., Perminova I.V. (2011): Structure of humic acids in zonal soils from ^{13}C NMR data. Eurasian Soil Science, 44: 976–983.

Knoblauch C., Beer C., Sosnin A., Wagner D., Pfeiffer E.-M. (2013): Predicting long-term carbon mineralization and trace gas production from thawing permafrost of North-East Siberia. Global Change Biology, 19: 1160–1172.

Komissarov M.A., Gabbasova I.M. (2014): Snowmelt-induced soil erosion on gentle slopes in the southern Cis-Ural region. Eurasian Soil Science, 47: 598–607.

Komissarov M.A., Gabbasova I.M. (2017): Erosion of agrochernozems under sprinkler irrigation and rainfall simulation in the southern forest-steppe of Bashkir Cis-Ural region. Eurasian Soil Science, 50: 253–261.

Krasilnikov P., Arnold R., Ibáñez J-J., Shoba S. (2009): A Handbook of Soil Terminology, Correlation and Classification. London, Routledge.

Lefèvre C., Rekik F., Alcantara V., Wiese L. (2017): Soil organic carbon – the hidden potential. Rome, FAO.

Mamontov V.G. (2002): Interpretation of water extraction data from saline soils. Methodical Manual. Moscow, Moscow Timiryazev Agricultural Academy. (in Russian)

Nicolás C., Hernández T., García C. (2012): Organic amendments as strategy to increase organic matter in particle-size fractions of a semi-arid soil. Applied Soil Ecology, 57: 50–58.

Orlov D.S. (1995): Humic Substances of Soils and General Theory of Humification. Boca Raton, CRC Press.

Orlov D.S., Grindel N.M. (1967) Spectrophotometric determination of humus in soil. Eurasian Soil Science, 1: 112–122.

Ovsepyan L.A., Kurganova I.N., Lopes De Gerenyu V.O., Kuzyakov Y.V., Rusakov A.V. (2020): Changes in the fractional composition of organic matter in the soils of the forest–steppe zone during their postagrogenic evolution. Eurasian Soil Science, 53: 50–61.

Piccolo A. (1996): Humus and soil conservation. In: Piccolo A. (ed.): Humic Substances in Terrestrial Ecosystems. Amsterdam, Elsevier: 225–264.

Polyakov V., Abakumov E. (2021): Assessments of organic carbon stabilization using the spectroscopic characteristics of humic acids separated from soils of the Lena River Delta. Separations, 8: 87.

Schimel D.S. (1995): Terrestrial ecosystems and the carbon cycle. Global Change Biology, 1: 77–91.

Semenov V.M., Tulina A.S., Semenova N.A., Ivannikova L.A. (2013): Humification and nonhumification pathways of the organic matter stabilization in soil: A review. Eurasian Soil Science, 46: 355–368.

Semenov V.M., Kogut B.M. (2015): Soil Organic Matter. Moscow, GEOS. (in Russian)

Six J., Conant R.T., Paul E.A., Paustian K. (2002): Stabilization mechanisms of soil organic matter: Implications for C-saturation of soils. Plant and Soil, 241: 155–176.

Sobol N.V., Gabbasova I.M., Komissarov M.A. (2015): Impact of climate changes on erosion processes in Republic of Bashkortostan. Arid Ecosystems, 5: 216–221.

Suleymanov A., Gabbasova I., Suleymanov R., Abakumov E., Polyakov V., Liebelt P. (2021): Mapping soil organic carbon under erosion processes using remote sensing. Hungarian Geographical Bulletin, 70: 49–64.

Swift R.S. (1996): Organic matter characterization. In: Sparks D.L., Page A.L., Helmke P.A., Loeppert R.H., Soltanpour P.N., Tabatabai M.A., Johnston C.T., Sumner M.E. (eds.): Methods of Soil Analysis. Part 3. Chemical methods. Madison, Soil Science Society of America, Inc.: 1011–1069.

Thompson S.O., Chersters G. (1970): Infrared spectra and differential thermograms of lignins and soil humic material saturated with different cations. Soil Science, 21: 265–272.

Trubetskoi O.A., Trubetskaya O.E. (2011): ^{13}C-NMR analysis of components of chernozem humic acids and their fractions with different molecular sizes and electrophoretic mobilities. Eurasian Soil Science, 44: 281–285.

Tsybulko H.H., Zhukova I.I., Yukhnovets A.V. (2005): Effect of fertilizers on the structural status of soddy-podzolic soil subjected to water erosion and the yield of agricultural crops. Agrochemistry, 6: 19–25. (in Russian)

Vadyunina A.F., Korchagina Z.A. (1986): Methods for Studying the Physical Properties of Soils. Moscow, Agropromizdat.

Vishnyakova O.V., Chimitdorzhieva G.D., Ayurova D.B. (2011): Structural changes in humic acids from arable chernozems and meadow-chernozemic cryogenic soils of Transbaikalia. Agrochemistry, 10: 3–8. (in Russian)

Wiesmeier M., Lungu M., Cerbari V., Boincean B., Hübner R., Kögel-Knabner I. (2018): Rebuilding soil carbon in degraded steppe soils of Eastern Europe: The importance of windbreaks and improved cropland management. Land Degradation & Development, 29: 875–883.

Yao S.-H., Zhang Y.-L., Han Y., Han X.-Z., Mao J.-D., Zhang B. (2019): Labile and recalcitrant components of organic matter of a Mollisol changed with land use and plant litter management: An advanced ^{13}C-NMR study. Science of the Total Environment, 660: 1–10.

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