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Conventional Tillage Effects on the Physico-Chemical Properties and Organic Matter of Chernozems Using ^{13}C-NMR Spectroscopy

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Abstract: In this study, we examined the influence of long-term conventional tillage on the water-physical, chemical properties, and composition of the organic matter of chernozems. The study has been conducted on an arable plot subjected to water and wind erosion in the Pre-Ural steppe zone (Republic of Bashkortostan, Russia). Soil samples were collected from non-eroded and eroded arable plots as well as from an adjacent pristine forest windbreak. Key structural fragments of soil organic matter under different land use types were identified and quantified using ^{13}C-NMR spectroscopy. The results showed that the water-physical properties deteriorated in agrochernozems: the number of valuable soil aggregates decreased and the soil bulk density increased, which may limit the growth of crops. The soil organic matter content for the different samples varied in the following direction: arable non-eroded > forest windbreak > arable eroded. It has been found that long-term plowing by conventional methods decreases aliphatic and increases aromatic structures in soils. As a result of the reduced inputs of plant residues, the processes of humification slowed down compared to unplowed soils. To increase soil fertility and carbon sequestration potential, it is necessary to stop degradation processes and implement conservation tillage practices.

Keywords: carbon sequestration; erosion; humic acids; nuclear magnetic resonance; ploughing; soil properties

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1. Introduction

Soil organic matter (SOM) is the most important factor in soil quality due to its effect on the soil chemical, physical, and biological processes. Croplands around the world undergo changes as a result of long-term use and, in most cases, due to improper management [1]. As a consequence, this has led to the depletion of soil resources, the development of degradation processes, the loss of soil organic carbon (SOC), and CO_2 emissions into the atmosphere [2]. Arable land is considered the most promising for SOC accumulation for climate change mitigation among other land uses [3]. With vast soil resources including fertile chernozems, Russia is among the top five countries with a high total additional annual SOC sequestration potential [4]. Despite the abandonment of large amounts of arable chernozems as a result of the collapse of the Soviet Union, extensive areas of agrochernozems have continued to be used for centuries, deteriorating the soil physical and chemical properties [5–9].

Agricultural use affects not only the quantitative but also the qualitative characteristics of SOM [10–14]. Ploughing the soil changes the hydrothermal conditions as well as the character and rates of input of SOM, which causes the transformation of the molecular structure of humic acids (HAs) [15]. Studies of HAs make it possible to determine the rates and limits of SOM loss under anthropogenic impacts. With the advent of high-precision methods such as ^{13}C-NMR spectroscopy, it became possible to accurately quantify the composition and structure of SOM. The ^{13}C-NMR spectroscopy method allows for the study of the structural and compositional features of the HA preparations, which provides a reliable assessment of the fundamental processes of humification and the composition of natural molecular-weight HAs [16,17].

The primary objectives of the present study were: (1) to examine the soil physical-chemical properties of long-term arable argochernozems and adjacent territory under forest windbreak; and (2) to study and compare the molecular composition of HAs isolated from different soils using ^{13}C-NMR spectroscopy analysis.

2. Materials and Methods

This study was conducted on an arable plot involved in agricultural use for at least 50 years. The study site is located in the southern forest-steppe zone of the Republic of Bashkortostan, Russia (Figure 1). The area of the study site is 200 hectares; the height above sea level varies from 165 m in the northwestern part to 195 m in the southeastern part. The cropland is characterized by ploughing with a turnover of the soil layer at a depth of 15–20 cm. In the year of field work and sample collection (2019), wheat (*Triticum aestivum*) was cultivated, while earlier in 2018, sugar beet was grown. The soil of the study site is represented by chernozem Calcic soils according to the WRB classification [18]. The study site is subject to the manifestation of water and wind erosion processes. In the northern and eastern parts, there are windbreaks to prevent the effects of wind erosion.

The climate of the region is warm-summer humid continental (Dfb), according to the Köppen climate classification [19], with a mean annual temperature of 2.8–3 °C. The mean January temperature is −15 °C, with an absolute minimum of −46 °C. The mean July temperature is +19 °C with an absolute maximum of +38 °C. Winter is characterized by steady frosty weather, snowfalls, and rare thaws. Summer is warm, with occasional rainfall. The mean annual precipitation is 450–550 mm [20].

The distribution of parent materials in the area is associated with the geological structure, the nature of the relief as well as the proximity to the floodplain terraces of the rivers. Predominant parent materials are mainly deluvial and eluvial-deluvial deposits [21].

We collected a total of 40 soil samples, 25 of which were taken from arable land and 15 from windbreaks from the topsoil (0–20 cm) during field work after harvest (October 2019). The cropland samples were taken from erosion-prone and undisturbed areas. The soil sampling work was conducted via a stratified simple random-sampling scheme. The approach was to randomly select soil samples from predetermined areas (arable undisturbed areas, arable erosion-prone, and pristine windbreaks). We used satellite data prior to fieldwork to identify erosion-prone and undisturbed areas. Erosion areas are well-identifiable from remote sensing data and are characterized by linear furrows and lighter areas due to shallow surface flow. Additionally, one non-eroded arable soil profile was opened up to the parent material and samples were collected from each genetic horizon (Ap, A1, AB, B). The erosion sediments (A0) and samples from the A1 horizon were collected from soils under a forest windbreak. Then, all of collected soil samples were air-dried, homogenized, sieved, and involved in subsequent laboratory analyses.

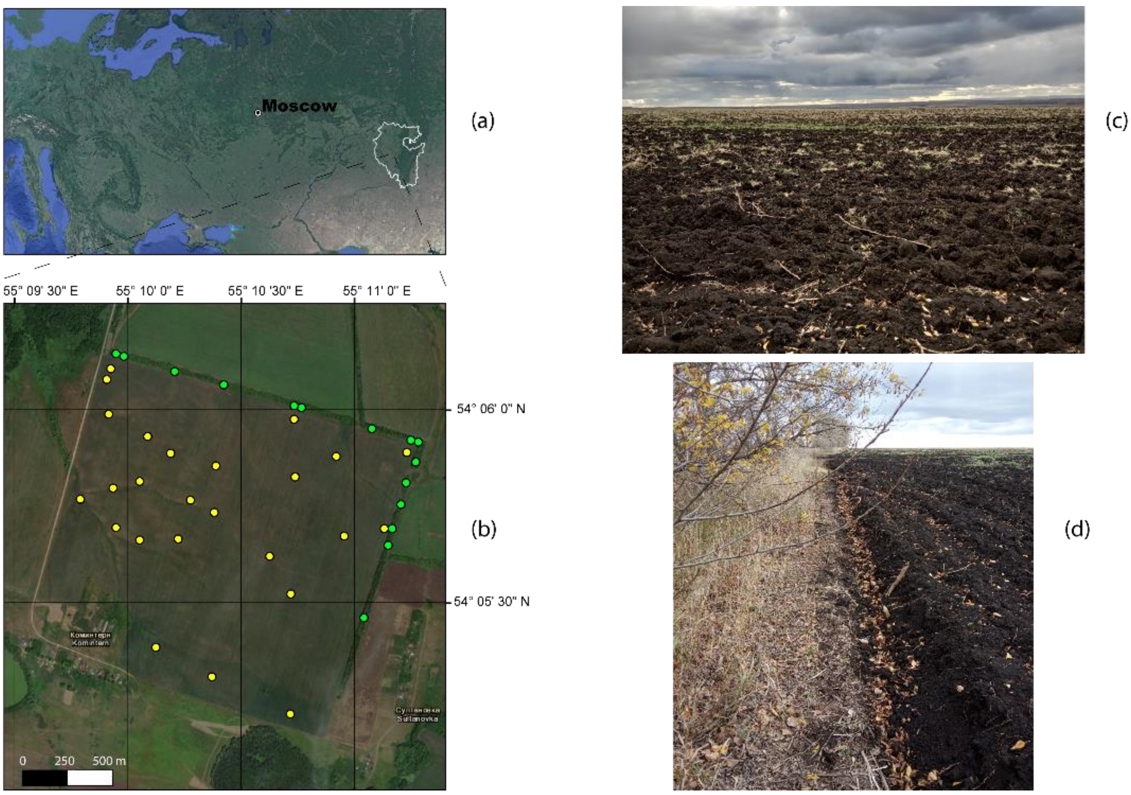

Figure 1. Maps and photos showing the location of the Republic of Bashkortostan (white boundary) (**a**); the studied arable plot location and sample points (white—arable, green—forest windbreak) (**b**); a general view of the field (**c**); and forest windbreaks (**d**). Sources: Google Maps.

Soil structure and texture measurements were performed according to the methodology of Vadyunina and Korchagina [22]. 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. Soil aggregate stability (wet sieving) was measured with a Baksheev device; the particle size distribution was conducted according to the Kachinsky "wet sedimentation" (pipette) method, which is the Russian analogue of analysis by Bowman and Hutka [23]. Aggregate condition was determined according to the coefficient of soil structure (Cst) (Equation (1)), where a value > 1.5 is classified as excellent; 1.5–0.67 as good, and 0.67 as unsatisfactory [22]. Aggregate stability was calculated by the sum of aggregates > 0.25 mm and classified as follows: <30%—unsatisfactory, 30–40—satisfactory; 40–75—good; and >75 as excessively high [22]. The Kachinsky dispersion factor (DF) characterizes the degree of the destruction of aggregates in water and was calculated as the ratio of particles (<0.001) of "microaggregate" silt to "granulometric" silt (Equation (2)) [22]. Soil penetration resistance was measured by repeating ten times from the soil surface to a depth of 45 cm in 2.5 cm intervals by using a soil compaction meter FieldScout SC 900 (Spectrum technologies, Aurora, IL, USA) equipped with a metal rod with a cone (size 1.3 cm). The assessment of the water-physical properties was performed for the non-eroded and pristine soil samples.

$$\mathrm{Cst} = \frac{\sum(10 - 0.25)}{\sum(> 10, < 0.25)} \quad (1)$$

where numbers are the sizes of the fractions (mm). In the numerator, the sum of fractions is from 0.25 to 10 mm; in the denominator, the sum of fractions is >10 and <0.25 mm.

$$\mathrm{DF} = \frac{a}{b} \times 100 \quad (2)$$

where *a* is the silt content in the microaggregate analysis (%) and *b* is the silt content in the particle size analysis (%).

Soil chemical analyses were carried out using the standard methods reported in [24,25]: the carbon (C) content, using the Tyurin method with termination according to Orlov and Grindel (Walkley-Black's analogue); available phosphorus (P_2O_5) and exchangeable potassium (K_2O), according to Chirikov; exchangeable cations (Ca^{2+} and Mg^{2+}) by the trilonometric method; and soil reaction by potentiometry (at 1 mol/L KCl suspension (1:2.5 soil/solution)). The content of available forms of ammonium ($N–NH_4$) and nitrate nitrogen ($N–NO_3$) were determined using a KCl solution. The gradation of SOM on the categories was carried out according to the scale [26], where content > 10% is characterized as "very high", 6–10%—"high", 4–6%—"average", 2–4%—"low", and <4%—"very low".

^{13}C-NMR spectroscopy was used to study HAs for five samples: arable (two eroded and two non-eroded) and one pristine sample from a forest windbreak. HAs from the aforementioned samples were extracted according to a published IHSS protocol [27] with modification by Vasilevich [28]. 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 the soil-solution of 0.1 N NaOH was poured into the sample with soil in a ratio of 1:10 and left for one day. Afterward, 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 HA from the solution, a 1 N H_2SO_4 solution was used in a ratio of 50 mL of acid/100 mL of supernatant 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.

Solid-state CP/MAS ^{13}C-NMR spectra of the HAs were measured with a Bruker Avance 500-NMR spectrometer (Billerica, MA, USA) in a 3.2-mm ZrO_2 rotor. The magic angle spinning speed was 20 kHz in all cases, and the nutation frequency for cross-polarization was u1/2p 1/4 62.5 kHz. Repetition delay was 3 s. The number of scans was 6500–32,000. The contact time used was 0.1–0.75 ms.

Table 1 shows the molecular fragments that we identified by CP/MAS ^{13}C-NMR spectroscopy: carboxyl (–COOR), carbonyl (–C=O), CH_3–, CH_2–, CH–aliphatic, –C–OR alcohols, esters and carbohydrates, phenolic (Ar–OH), quinone (Ar=O), aromatic (Ar–).

Table 1. Chemical shifts of atoms of the ^{13}C molecular fragments of HAs.

Chemical Shift, (ppm)	Type of Molecular Fragments
0–46	C, H-substituted aliphatic fragments
46–60	Methoxy and O, N-substituted aliphatic fragments
60–110	Aliphatic fragments doubly substituted by heteroatoms (including carbohydrate) and methine carbon of ethers and esters
110–160	C, H-substituted aromatic fragments; O, N-substituted aromatic fragments
160–185	Carboxyl groups, esters, amides, and their derivatives
185–200	Quinone groups; groups of aldehydes and ketones

The reliability of changes in the soil properties was assessed using the Student's test. The significant differences between the soil properties were assessed by the least significant difference (LSD) of analysis of variance (ANOVA). Differences at the $p < 0.05$ level were reported as statistically significant. Statistical analysis including mean and standard deviation values was performed using R 4.0.4 [29] and RStudio (version 1.3.1093, Boston, MA, USA) [30].

3. Results

3.1. Morphological Description of Study Soil

The arable soil profile was differentiated into four genetic horizons typical for these soils (Ap, A1, AB, B) [21]. In all horizons, starting from the surface (Ap), there was effervescence in reaction with 10% HCl. The top Ap (0–20 cm) horizon was surface humus horizon transformed by conventional tillage. The Ap was an almost black cultivated layer, medium moisture, powdery lumpy, heavy loam, with roots, the transition to the underlying layer was clear. The underlying horizon A1 (20–38 cm) was characterized by a dark gray color, weak moisture, small-grained, heavy loam, the presence of small roots, and clear color transition. The AB (38–67 cm) layer was brownish gray, weak moisture, large-grained, heavy loam, medium compacted, mycelium carbonate, and had a smooth transition in color. The B (67–75 cm) layer was characterized by a yellow-brown color, medium moisture, granular-lumpy, heavy loam, medium compacted, and mycelium carbonate.

3.2. Water-Physical Properties of Study Soils

The analysis of the structural and soil aggregate composition for genetic horizons (Ap, A1, AB, B) and erosion sediment (A0) is presented in Table 2. Aggregates larger than 10 mm (22.4–35.4%) prevailed in the arable soil layer (Ap) and soil horizon A1 of uneroded chernozems, while in the AB and B soil horizons, fractions of 5–3 mm (24.6%) predominated. Fractions 10–7 mm in size predominated in the soil samples under the forest windbreak (19.7%). The content of agronomically valuable aggregates (0.25 to 10 mm) in the soil under the forest was 61.5%, which was slightly higher than in the agrochernozems (57%). The amount of water-stable aggregates >0.25 mm in the arable layer averaged 58.6%, which characterized the soil structure as "good" [22]. In the AB and B soil horizons, the content of these fractions increased with 80.2 and 77.5%, respectively. This value was 53% in the sample under the forest windbreak in the A1 layer, which also characterized the structure as "good" [22].

Table 2. The structural and aggregate composition of the soils (mean + SD) [1].

Horizon (Depth, cm)	Particle Size, (mm); Content, (%)								Structural	Σ	0.25–10
	>10	10–7	7–5	5–3	3–1	1–0.5	0.5–0.25	<0.25	Water-Stable		>0.25
Arable non-eroded											
Ap (0–20)	35.4 ± 2.2	12.6 ± 1.1	9.8 ± 0.8	10.7 ± 0.8	8.6 ± 0.8	8.1 ± 0.8	7.2 ± 0.5	7.6 ± 0.5	1.3		57
			0.36 ± 0.5	0.8 ± 0.7	4.6 ± 0.4	15.8 ± 0.7	37.1 ± 1.9	41.4 ± 2.1	0.6		58.6
A1 (20–38)	22.4	13.1	12.1	12.7	10.4	10.5	9.1	9.7	2.1		67.9
			0.2	0.6	4.9	15.5	33.5	45.3	0.6		54.7
AB (38–67)	4.6	7.6	13	24.6	18.6	15.6	9.4	6.6	7.9		88.8
			1.2	7.2	34.9	17.1	19.9	19.8	0.9		80.2
B (67–75)	9.2	9.9	12.6	24	15.8	12.9	8.2	7.4	5		83.4
			2.4	9.8	30.9	14.2	20.3	22.5	0.8		77.5
Forest windbreak											
A0 (0–2)	3.7	3.2	2.9	4.0	2.7	75.1	5.8	2.6	14.9		93.7
		1.6	0.5	1.2	1.9	2.9	26.4	65.6	0.4		34.4
A1 (2–20)	34.2 ± 1.8	19.7 ± 1.2	14 ± 0.6	13.6 ± 0.5	6.8 ± 0.3	4.6 ± 0.4	2.8 ± 0.3	4.3 ± 0.4	1.6		61.5
			0.4 ± 0.6	1.4 ± 0.4	7 ± 0.5	11.4 ± 0.6	32.7 ± 1.8	47.1 ± 2.1	0.6		52.9

[1] Above the line are structural aggregates, below the line are water-stable aggregates.

Fractions sized 0.05–0.01 mm (coarse dust) prevailed in all soil samples, according to particle size distribution, while it was 0.25–0.05 mm (fine sand), according to the microaggregate composition (Table 3). The content of physical clay particles (<0.01) in the arable top soil horizons (0–20 and 20–38 cm) was 50.1–51.5%; in the lower part of the profile, it did not change. In the A1 soil horizon of the forest windbreak sample, these values were lower (44.5%), while the silt content (<0.001 mm) in the surface soil layer for all samples was at the same level (28.3–29.9%). The granulometric composition of all arable soil horizons was classified as heavy loam, while the pristine sample was classified as medium loam. The structure coefficient and the dispersion factor were higher in the arable soil samples (96.2 and 14.9, respectively), while the values were 85.7 and 9.8 under the forest windbreak soils.

Table 3. Particle size distribution of soils (mean + SD) [1].

Horizon (Depth, cm)	Particle Size, (mm); Content, (%)							Cst	Dispersion Factor (DF)	Granulometric Composition
	1–0.25	0.25–0.05	0.05–0.01	0.01–0.005	0.005–0.001	<0.001	<0.01			
Arable non-eroded										
Ap (0–20)	3.8 ± 0.4	11.6 ± 0.7	33.1 ± 1.5	10 ± 0.8	11.6 ± 0.8	29.9 ± 1.7	51.5 ± 2.3	96.2	14.9	Heavy loam
	10.3 ± 0.8	49.2 ± 2.6	24.3 ± 1.4	7.7 ± 0.4	4.1 ± 0.3	4.5 ± 0.2	16.2 ± 1.3			
A1 (20–38)	6.4	10.8	32.7	7.4	11.6	31.2	50.2	106.8	9.1	Heavy loam
	15.9	46.8	23.9	6.1	4.5	2.8	13.4			
AB (38–67)	1.7	12	29.7	8.3	11.8	35.6	55.6	124.9	15.9	Heavy loam
	19.4	47.8	19	4.5	3.7	5.7	13.8			
B (67–75)	2.3	17.2	30.9	9.8	8.8	31.1	52.7	98.0	18	Heavy loam
	13.9	55.7	14.8	4.8	5.2	5.6	15.6			
Forest windbreak										
A0 (0–2)	5.1	10.1	37.6	7.8	10.4	29	52.3	86.7	9.8	Heavy loam
	10	57.6	21.1	5.3	3.2	2.8	11.3			
A1 (2–20)	5.6 ± 0.4	13.2 ± 1.1	36.8 ± 2.2	7 ± 0.8	9.2 ± 1.0	28.3 ± 2.4	44.5 ± 2.6	85.7	11.4	Medium loam
	10.5 ± 2.3	54.9 ± 2.6	18.9 ± 1.7	8.1 ± 0.8	4.4 ± 0.3	3.2 ± 0.4	15.7 ± 1.4			

[1] Above the line are the particle size distribution, below the line are the microaggregate distribution.

Figure 2 shows the vertical distribution of the soils' penetration resistance under arable (non-eroded and eroded) and forest windbreak plots. Values of penetration resistance in arable soil samples, depending on erodibility were similar up to a depth of 40 cm: there was a sharp jump to 1760 ± 64 kPa to a soil depth of 10–15 cm and then a smooth increase. However, the resistance values of the eroded soil samples, on average, exceeded the non-eroded counterparts, reaching significant changes at the defined level of significance at a soil depth of 40 to 45 cm (2500 ± 88 and 1850 ± 70 kPa, respectively). Resistance values for soil samples under the forest to a soil depth of 20 cm were lower than their arable counterparts, but from a soil depth of 23–24 cm, there was an increase in resistance to 3000 ± 41 kPa. The significant changes for forest compared to the arable values were found at almost all depths at the defined level of significance.

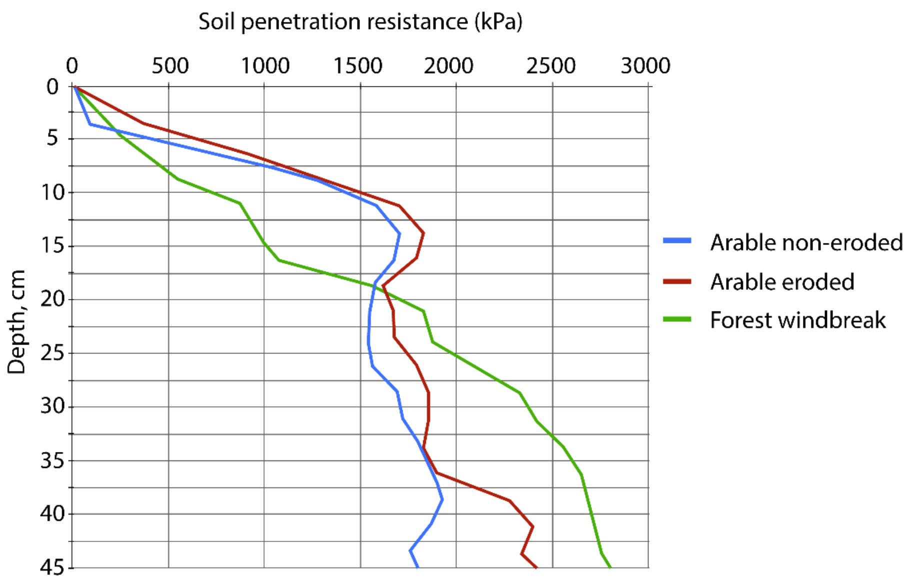

Figure 2. Vertical distribution penetration resistance of soils under arable and forest plots (mean values for 10 replicates for each soil type).

Water-physical properties of the chernozem soils are presented in Table 4. The percentage of hygroscopic moisture and maximum hygroscopic content in the arable horizons were 9.5 and 12.7%, respectively, while in the forest counterparts, they were 3.6 and 8.2% in the top soil layer, respectively. The wilting point and specific surface area of agrochernozems were also higher compared to the forest samples.

Table 4. Water-physical properties of the study soils (mean + SD).

Horizon (Depth, cm)	Hygroscopic Moisture, (%)	Maximum Hygroscopic Moisture, (%)	Wilting Point, (%)	Soil Specific Surface, (m^2/g)
		Arable non-eroded		
Ap (0–20)	4.3 ± 0.5	9.5 ± 1.5	12.7 ± 1.7	37.8 ± 2.6
A1 (20–38)	4.4	9.9	13.2	39.4
AB (38–67)	4.3	10	13.3	39.8
B (67–75)	3.3	7.9	10.6	31.8
		Forest windbreak		
A0 (0–2)	4.1	8.7	11.7	35
A1 (2–20)	3.6 ± 0.4	8.2 ± 0.6	10.9 ± 0.7	32.6 ± 2.2

3.3. Chemical Properties of Soils

Table 5 shows the chemical properties of soil samples of non-eroded arable and forest soils. All investigated soil horizons were characterized by a neutral reaction pH H_2O of 6.8–7.1. The SOM content in the 0–20 cm uneroded arable sample was 7.9% and decreased to 2.5% with soil depth (B horizon). The concentration of SOM in the A1 soil horizon sample under the forest vegetation was 5.3%. In the erosional sediment (0–2 cm), formed as a result of redeposition due to wind erosion, the SOM content was 5.9%. The content of $N–NO_3$ was 3–4 times lower in the forest soil samples compared to arable land. In the agrochernozem soil, these values in the top soil horizons (Ap and A) were 22.4–24% and decreased sharply with depth. The $N–NH_4$ values in the study samples were more similar, with a slight predominance in the arable counterpart. The P_2O_5 content at 0–20 cm in the forest sample was 59 mg kg^{-1} soil, which was lower than in the arable land (81 mg kg^{-1} soil), whereas the K_2O content was higher in virgin soils. The amount of adsorbed cations was higher in the arable soil, among which Ca^{2+} exceeded Mg^{2+}.

Table 5. Chemical properties of the chernozem soils.

Horizon (Depth, cm)	pH (H_2O)	SOM, (%)	$N–NO_3$	$N–NH_4$	P_2O_5	K_2O	Ca^{2+}	Mg^{2+}
			mg kg^{-1} soil				$cmol_{(+)}$ kg^{-1}	
			Arable non-eroded					
Ap (0–20)	6.9	7.9	22.4	18.2	81	120	24.0	3.7
A (20–38)	6.9	7.5	24.0	22.1	56	95	23.5	3.2
AB (38–67)	6.8	5.2	12.3	10.1	31	90	23.4	4.3
B (67–75)	7.1	2.5	13.2	3.4	21	75	18.9	4.5
			Forest windbreak					
A0 (0–2)	7.1	5.9	8.3	16.2	77	150	21	3.5
A1 (2–20)	6.9	5.3	4.6	16.6	59	155	18.4	2.8

Figure 3 shows the average values of the SOM, pH, and exchangeable cations in the 0–20 cm soil layers at all study sites, with the arable soil samples divided into eroded and non-eroded samples. The mean values for SOM ranged from 6.1 to 7.1% depending on the land use type. Obviously, the lowest SOM content was observed on plots prone to water erosion (6 ± 1.2%). This trend was found to be statistically significant at the defined level of significance. The studied soils in the top layer were characterized by a neutral reaction, where the values did not statistically differ between soils. The Ca^{2+} content ranged from 28.3 to 41.5 $cmol_{(+)}$ kg^{-1} depending on the soil type and was statistically different for the eroded soils. The content of adsorbed cations was also higher in the pristine ecosystems, while the lowest values were found in the eroded samples. There were no significant differences observed in the Ca^{2+} and Mg^{2+} contents among the non-eroded and forest soils, however, the eroded soils were characterized by lower values.

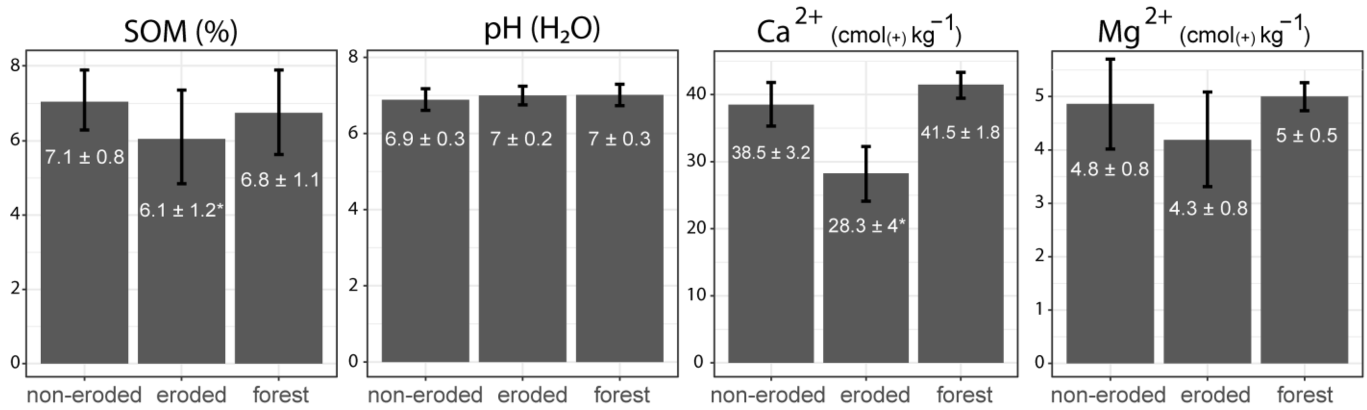

Figure 3. Variation and mean values of SOM, pH, Ca and Mg contents in the top soil layer (0–20 cm) among the arable (non-eroded and eroded) and forest soils. * Significant changes in the chemical properties were observed ($t_{emp} > t_{tbl}$ at $p \leq 0.05$); in other cases, the changes were not significant ($t_{emp} \leq t_{tbl}$ at $p \leq 0.05$).

3.4. Characterization of HAs by ^{13}C-NMR Spectroscopy

The spectra obtained from the ^{13}C-NMR spectroscopy are presented in Figure 4. The following parameters were used to standardize the quantitative characteristics of the HA macromolecules: the ratio of C of the aromatic structures to aliphatic, degree of decomposition of SOM (C-alkyl/O-alkyl), and the integral indicator of the hydrophobicity of HAs (AL h, r + AR h, r). The distribution of C by structural fragments in HAs (% of total C) showed major peaks in the spectra 0–47 (Alkyl C), 60–110 (CAlk-O, CO-Alk-O), and 110–160 (Aryl C). The HA spectra of the studied arable soil samples (Nos. 1–4) were very similar to each other, despite the fact that some of them were eroded (Nos. 3, 4). The signal in the region of C, H-substituted aliphatic fragments (0–46) was more pronounced in the HAs of the unploughed sample than in the agrochernozem. The forest sample (No. 5) had a dominant peak in the Alkyl C region, whereas the arable samples had a significant peak in the Aryl C region.

Percentage of C in the main structural fragments of HAs is shown in Table 6. In the studied humic preparations of the surface soil layer of arable samples, the content of the functional groups of the HA structural fragments was similar, with some predominance of the latter (51–53%). The HA spectrum of the soil samples in the forest (No. 5) was characterized by the highest content of aliphatic (58%) and the lowest proportion of aromatic functional groups (47%) (AR/AL ratio—0.72). The forest soil samples were characterized by the highest degree of humification (0.85). According to the integral index, non-eroded soils showed a greater degree of hydrophobicity and humification compared to their eroded counterparts.

Table 6. Percentage of C in the main structural fragments of HAs from the studied surface soil horizons [1].

	Chemical Shifts in % from ^{13}C											
No.	0–47	47–60	60–110	110–160	160–185	185–200	AR	AL	AR/AL	AL h, r + AR h, r, (%)	C,H-AL/O,N-AL	SOM, (%)
1	22	6	22	35	12	3	47	53	0.89	57	0.77	7.3
2	21	6	20	38	12	3	49	51	0.96	59	0.78	6.8
3	20	7	23	35	12	3	47	53	0.89	55	0.66	5.8
4	22	7	22	35	12	3	47	53	0.89	56	0.75	6.6
5	25	7	22	31	12	3	42	58	0.72	56	0.85	6.5

[1] 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.

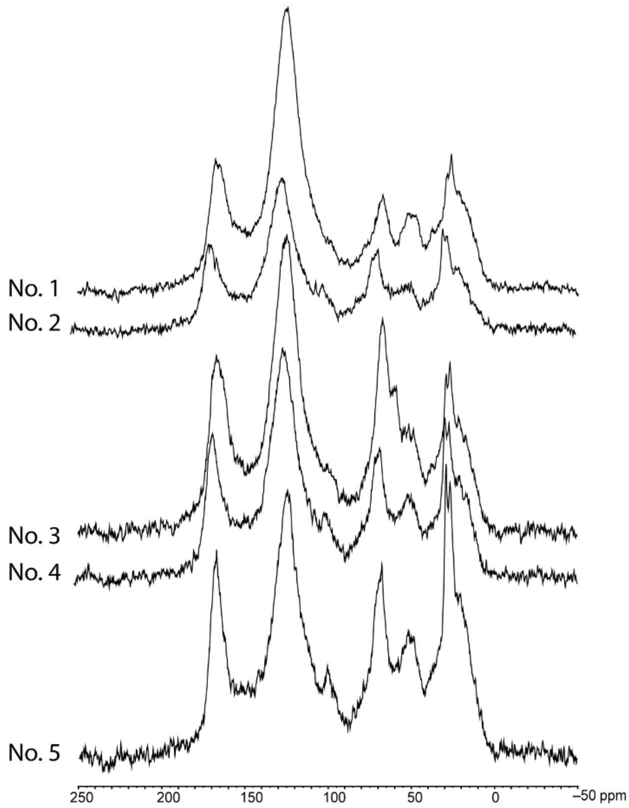

Figure 4. ^{13}C CP/MAS-NMR spectroscopy of HAs extracted from: arable non-eroded chernozem (Nos. 1, 2), arable eroded chernozem (Nos. 3, 4), forest windbreak chernozem (No. 5). X-axis—chemical shifts, ppm.

4. Discussion

The studied soils have undergone changes as a result of long-term conventional tillage, fertilization, and the application of various ameliorative and agronomic practices. Deterioration in the water-physical properties due to conventional tillage all over the world has been shown in numerous articles [31–35] including for chernozems [36–38]. For example, Trofimova [39] previously showed that the number of agronomically valuable soil aggregates in the 0–30 cm soil layer of chernozems (ordinary and leached) under fallow and forest windbreaks exceeded the number under different systems of treatment: combined, shallow mulching, and zero tillage. Similarly, in the study of Schein [40] on arable chernozems of the European part of Russia, the content of agronomically valuable soil aggregates under fallow land was higher, while the content of physical clay and silt fractions in the arable-fallow system was similar, which is comparable with our results.

Significant difference in the penetration resistance between the arable and virgin soil samples was due to prolonged exposure to heavy agricultural equipment and traditional tillage with a plough with a layer turnover. This anthropogenic impact led to the formation of a plough sole about 10 cm thick. The formation of a plough sole contributes to the deterioration of the physical properties of soils, disrupting the movement of water, nutrients and the development of erosion processes [41–43]. Medvedev [37] showed that medium- and heavy-loam soils are more prone to the formation of a plough sole. Since the surface soil layer is where most of the roots of crops occur (sugar beet and wheat), further deterioration by soil compaction will lead to growth limitation. For example, according to Kees [44], at values already around 1500 kpa, there is a decrease in the root growth of most crops, while at 2500 kpa, the root growth of many plants stops.

In our study, the SOM content varied in the following direction: non-eroded cropland > forest windbreak > eroded cropland. All soils were characterized by "high" levels of SOM, despite erodibility and different types of land use. SOM content was lower under forest compared to arable non-eroded, which can be explained in different ways. The surface layer of soils under the forest is overlain by erosion material with a thickness of 2 to 10–15 cm transferred from the arable land due to eolian processes. The formed layer limits the flow of plant remains in the buried humus-accumulative horizon. Such conditions lead to processes of diagenesis of the labile part of the SOM and a slight decrease in its total content [45,46]. On the other hand, Baeva [47] reported that when the natural-climatic zones changed from north to south, the difference between the organic C content in arable and pristine soils decreased, which may be related to the lower productivity of meadow vegetation in the steppe zones. Additionally, taking into account the high SOM content in arable non-eroded plots, we can conclude that chernozem soils are more resistant to anthropogenic influences [48]. For example, no difference was previously found between the SOM content in fallow and arable plots of chernozems [40]. Additionally, there is a possible influence on the maintenance of soil fertility by changing the composition of crops in the rotation [49].

Reduced values of the SOM content in arable plots compared with pristine counterparts are characteristic of most soils as a result of conventional ploughing. A number of studies have reported a deterioration in fertility and a decrease in SOC content on arable chernozems in European Russia [5,6,9]. A similar trend was observed on chernozems in the study region (Pre-Ural forest-steppe zone). Previously, it was found that the SOM content on virgin Haplic chernozems and Luvic chernozems exceeded their arable counterparts using turnover ploughing [50].

Arable lands of the Pre-Ural steppe zone are subject to the influence of erosion processes, which limits their fertility [21]. Involvement in arable farming with conventional tillage methods has contributed to the accelerated development of degradation processes, especially the intensification of processes of water and wind erosion. The average SOM values of eroded arable soil samples were lower than non-eroded samples by 1%, which is associated with the deflation and washout of silty and fine-grained soil fractions. The eroded soils were also characterized by a lower content of adsorbed cations.

According to ^{13}C-NMR spectroscopy, the distribution of C in structural fragments in HAs (% of C total) corresponds to the previously studied chernozems [51–53] including arable lands [54] (Table 6). Chemical shifts 110–160 (aromatic C) were the most pronounced of all the samples studied, caused mainly by the influence of lignin and tannins. We also did not exclude the degradation of the SOM and the selection of the most stable functional groups, in this case, aromatic fragments. However, this value was markedly lower (31) in the soil samples under the forest windbreak, which may be related to the processes of the humification of organic residues and the formation of aliphatic fragments, which prevailed over aromatic ones. However, it was previously noted that the content of aromatic fragments was slightly higher in the soils of the meadow ecosystems and significantly lower in the upper horizons of the soils of forest ecosystems [55]. This is the result of the increased content of C alkyl forms in the HA molecules of soils formed under forest.

In our study, the differences between the arable and non-arable samples (under the forest windbreak) were revealed. It was found that the involvement of virgin chernozems in arable farming resulted in a decrease in aliphatic fragments. The AR/AL ratio was lower in the arable samples, which may be explained by microbiological destruction of the hydrolyzable aliphatic part of humic substances due to the conventional tillage system (ploughing) and, accordingly, the lack of conditions for the accumulation and decomposition of plant residues. Similar results were reported in other works on the study of arable chernozems. A number of studies have revealed a decrease in the amount of aliphatic chains and an increase in the content of aromatic structures and carboxylic groups [15,53]. Identical results have been reported in other climatic zones. For example, Lodygin and Abakumov [11] reported that agricultural development of Eutric Albic Retisols (Loamic) led to a transformation in the HA molecular structure, which was demonstrated by a relatively higher fraction of aromatic molecule fragments and a decrease in the number of carbonyl groups. Thus, we can assume that long-term conventional tillage leads to an increase in the content of aromatic fragments and, accordingly, a decrease in aliphatic compounds.

The HAs of the eroded and non-eroded soils were similar, although a more marked difference was previously found between the eroded and non-eroded arable chernozems. It was shown that the soil samples not subjected to erosion had more aromatic fragments compared to the eroded soil samples [54]. In general, the HA structure of the studied soils corresponds to the soils of the forest-steppe zone, indicating the similarity of the biothermodynamic conditions of humus formation in these soils [56].

Switching to conservation tillage systems is seen as a rational way to improve soil fertility. Previous studies have concluded that reduced tillage enhances SOM stabilization during the transition from cropland to grassland and vice versa [12,48]. For example, Shrestha [13] reported a predominance of O-alkyl C in soils under no-till compared to conventional tillage, suggesting a more advanced stage of SOM decomposition. Similarly, no-till promoted the formation of stable HAs with a higher proportion of aliphatic and hydrophobic compounds, while the hydrophobicity of aliphatic fragments in HAs improved the stability of C [57]. Previously, it has been reported that the use of long-term conservation tillage and grain–fallow–grass crop rotation practices (zero till) improved the physical and chemical properties of soils and contributed to reducing the activity of erosion processes in the study region (Republic of Bashkortostan) [50,58]. Thus, the most expedient is considered to be the transfer of arable land to fallow land, or a change of agricultural practices to conservation practices. We imply that the transition to no-till tillage will reduce erosion, and improve the physical and chemical properties of agrochernozems and C sequestration.

5. Conclusions

The presented study demonstrated changes in the water-physical and chemical properties of arable chernozems as a result of agrogenic influence in the Pre-Ural steppe zone. A comparison of arable soils with the use of long-time conventional tillage methods and undisturbed soils under forest windbreak obtained the following conclusions:

1. The long-term use and conventional tillage of chernozem soils caused a deterioration in the water-physical properties in the surface layer. The number of agronomically valuable soil aggregates decreased and the content of large soil aggregates increased. The granulometric composition of agrochernozems changed from medium loam to heavy loam. As a result of ploughing, the water-holding capacity of the soil structure also deteriorated. Resistance to penetration in the top soil layer of arable chernozems was higher due to prolonged exposure to heavy machinery, which can create limitations for root development and access to nutrients.
2. The SOM content in uneroded arable and pristine soils were comparable. As a consequence of water erosion processes, the SOM content in the eroded plots was 1% lower compared to their non-eroded counterparts. The low content of exchangeable cations was also noted in these samples.
3. The ^{13}C-NMR results of the studied soils demonstrated differences between the arable and non-arable samples. Anthropogenic impact reduced aliphatic and increased aromatic structures compared to virgin land as well as inhibited the humification processes. Chemical shifts 110–160 (aromatic C) were the most pronounced of all the samples studied. No significant difference was found between the eroded and non-eroded arable samples.
4. Based on the data obtained, we can conclude that despite the deterioration of some properties, chernozems have a higher resistance to degradation compared to other soils. The main factors of deterioration of properties are a reduction in plant residues in the soil, the intensification of the mineralization of SOM, erosion, and deflation due to mechanical treatment. We hypothesize that erosion-prone areas have the greatest C sequestration potential. To increase the fertility and SOM content, first of all, it is necessary to introduce soil-protective techniques to stop erosion processes. The

introduction of soil conservation practices such as zero tillage is considered as one of the most rational solutions to improve the water-physical properties and increase the amount of N and SOC.

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