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AGRICULTURAL CHEMISTRY AND SOIL FERTILITY

Changes in the Agrochemical Properties of Dark Gray Soil in the Western Ukrainian Forest-Steppe under the Effect of Long-Term Agricultural Use

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Abstract—The changes in the properties of dark gray forest soil in the Ukrainian Western Forest-Steppe under the effect of long-term agricultural use in a grain–row crop rotation without fertilization and with the application of mineral and organomineral complex fertilizers have been studied. The changes in the morphological properties of the soil, the reaction of the soil solution, the total and exchangeable acidities, the total exchangeable bases, the degree of base saturation, and the content and reserve of organic carbon over a 50-year-long period of plowing have been studied using different methods. It has been found that the acidification of the upper layer was intensified and the content of organic matter and the degree of base saturation decreased during the period studied (1961–2010). The effect of the management practice on the evolution and dynamics of the soil degradation has been studied. It has been shown that the cultivation of soils without fertilization primarily resulted in a decrease in the humus content; the application of mineral fertilizers increased the acidity of the soils.

Keywords: high-input soil management, fertilizing system, reaction of the soil solution, soil degradation

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INTRODUCTION

The technogenic and energy loads on arable soils have abruptly increased since the mid-20th century. Under the administrative system of economic management, the predominant farming systems resulted in an increase in the anthropogenic load on agrocenoses [16, 21].

The anthropogenic use of soils affects their chemical, physical, agrochemical, and morphological properties at all the organization levels of the soil profile [8]. These changes allow tracing the accelerated evolution of soils [22].

About 22% of the agricultural land in Europe has decreased productivity, including 7.7% because of agrochemical degradation, and the degradation has been significantly accelerated in the last 50 years [24, 25].

The negative manifestations of the agrochemical degradation of land include the imbalance of nutrients; the deterioration of the physical properties; the acidification or alkalization, dehumification, salinization, and leaching of micro- and macronutrients; and the conversion of nutrients to unavailable forms [23].

Changes in the agrophysical properties (compaction of the plow and subsurface layers) are most frequently observed in arable soils; they affect the structure of the pore space and the water permeability of soils. The increase in the anthropogenic load on soils (including gray forest soils) can provoke their agrochemical degradation: an increase in the acidity of the plow layer, changes in the composition of the exchangeable cations and degree of base saturation, and dehumification. The rate and evolution of the degradation directly depend on the degree and duration of the anthropogenic impact [9, 19, 22].

The agricultural use of the major area in the Ukrainian forest-steppe zone with a high anthropogenic load for a long time period has significantly affected the composition, properties, and regimes of the arable soils [3]. Fertilization is one of the most significant factors of the anthropogenic impact on the soil cover. Fertilizers also affect the agroecological status and properties of arable soils and create additional (frequently unpredictable) pressure on the entire agroecosystem. The intensification of cultivation technologies is accompanied by an increase in the crop yield, which increases the removal of nutrients from the soil and, hence, creates their negative balance in the crop rotation, which is of special importance in an open cycle of agricultural production.

Previously, this problem was solved by the permanent (frequently imbalanced) and scientifically ill-founded increase in the application rates of fertilizers and other chemicals, which resulted in irreversible changes in the soil environment. The agrochemical implications of the long-term application of mineral and organic fertilizers include the deterioration of the agrochemical, physicochemical, and other properties of the fertilized soils. Most mineral fertilizers are physiologically acidic; therefore, their long-term application at high rates is frequently accompanied by soil acidification [12].

According to Filon et al. [20], the long-term application of mineral fertilizers increases the exchangeable and total acidities and decreases the base saturation of dark gray soil. These negative processes at the regular and long-term application of fertilizers to arable lands are due to not only the physiological acidity of fertilizers but also to the enhanced removal of biophilic elements (including calcium) from the soil because of the increase in crop yield. The use of a mineral fertilizing system results in the structural damage of soils, an increase in their bulk density, and a decrease in porosity [15]. The long-term production use of soils without application of organic fertilizers also decreases the content of humus or, at best, allows maintaining its initial level [11].

According to some authors [10, 11, 14], the negative effect of mineral fertilizers on the physicochemical parameters of soil can be balanced by the application of organic fertilizers. This is an important means for preventing the dehumification of soils. All fertilizing systems can be ranked in accordance with their efficiency for the restoration of the humus reserves: mineral fertilization—organic fertilization—organomineral fertilization [10]. At the same time, fertilizers are among the most important anthropogenic factors affecting the soil humus status [13].

The current economic conditions of the country also affected the agroecological status of soils. The general tendencies toward decreasing livestock development and reducing cattle stock, which had been observed since the second half of the 1990s, reached catastrophic levels in the last years. The decline or even total liquidation of large livestock units resulted in an abrupt reduction of organic fertilizer application in crop rotations. The lack of financial resources for some land users and the negligence of others resulted in a general reduction of chemical reclamation, including the liming of acidic soils.

These conditions aggravate the agrochemical and physicochemical degradation of soils, and the studies related to the ecology and economics of fertilization increased more in urgency.

OBJECT AND METHODS OF STUDY

Studies were performed in Rovno oblast; podzolized sandy loamy dark gray soils typical for the Ukrainian western forest-steppe were studied. Field observations were made in the area of the Field Research Station of the Institute of Agriculture of the Western Poles'e. Laboratory studies were conducted at the Department of Agrochemistry, Soil Science, and Agriculture of the National University of Water Management and Nature Resources Use.

The field station was established in 1961; the initial state of the soil was fixed by the establishment of 12 key soil profiles; soil samples were taken, and their physical, water-physical, and agrochemical properties were determined. A soil survey of the entire station area was also performed using a series of accessory profile pits, and detailed soil maps were made.

Since 1961, a long-term experiment with a grain–row crop rotation has been conducted at the station; the rotation cycle has continued for nine years. A developed fertilizing schedule was used in the field experiment and included the following treatments: (1) the control (without fertilizers), (2) a mineral fertilizing system (N72P64K65), and (3) an organomineral fertilizing system (manure at 10 t/ha + N72P64K65).

The program of studies at the station involved permanent agrochemical, phonological, and meteorological observations.

In the next studies, three treatments were used: the control (without fertilizers throughout the period of the observations), a mineral fertilizing system, and an organomineral fertilizing system [13].

In 2010, additional soil profiles were established on the plots of all three treatments, where initial the profiles were established in 1961.

Agrochemical studies were performed using the following methods: the soil solution reaction was determined by potentiometry, the hydrolytic and exchangeable acidities were determined by the Kappen method, the degree of base saturation was determined by the Kappen–Hillkowitz method, and the organic carbon was determined by the Tyurin method.

The aim of the work was to study the effect of long-term agricultural use of dark gray soil under different fertilizing systems on the agrochemical and physicochemical parameters of the soil in the context of the general changes in the soil–climatic conditions of the area.

RESULTS OF STUDY

The study of the soil profiles in the treatments at the field station showed that the soils reflect the features of both soddy (well-developed humus horizon, the presence of moles and lime nodules) and podzolic (leaching of carbonates from the upper horizons and the transfer of colloids to the lower layers, which resulted in the differentiation of the soil profile into the horizons of colloidal eluvium and illuvium) pedogenesis types.

The general structure of the soil profiles is as follows (the horizon depths are averaged as of November of 2010):

Ap (0–35 cm), plow humus horizon formed by the mixing of the original A1A2 horizon with partial disaggregation and compaction because of the mechanical

Table 1. Occurrence depths of the lower boundaries of the genetic horizons in the studied soils, cm (the mean value and variation range are given above and under the line, respectively)

Profile	Genetic horizon				
	A1A2/Ap	A2B	B1	B2Ck	Ck
			Original soil, 1961		
1	35.2 ± 0.19 / 35.0–35.5	70.2 ± 0.45 / 69.5–70.7	130.4 ± 0.38 / 130.0–131.0	150.5 ± 0.36 / 150.0–151.0	>150.5 / 150.0–151.0
2	33.7 ± 0.51 / 33.1–34.5	68.4 ± 0.19 / 68.2–68.7	127.3 ± 0.34 / 127.0–127.9	147.3 ± 0.35 / 146.9–147.9	>147.3 / 146.9–147.9
3	36.9 ± 0.56 / 36.5–37.5	71.6 ± 0.54 / 70.6–72.2	130.6 ± 0.41 / 129.5–131.0	151.0 ± 0.53 / 150.5–152.0	>151.0 / 150.5–152.0
			2010		
1	33.4 ± 0.36 / 33.0–34.0	72.0 ± 0.56 / 71.0–72.7	130.3 ± 0.53 / 130.0–131.0	150.4 ± 0.49 / 150.0–151.0	>150.4 / 150.0–151.0
2	34.2 ± 0.54 / 33.6–34.9	81.7 ± 0.38 / 81.3–82.4	135.2 ± 0.41 / 134.7–135.9	168.3 ± 0.36 / 167.8–168.9	>168.3 / 167.8–168.9
3	37.4 ± 0.29 / 37.0–37.8	80.4 ± 0.37 / 80.0–81.0	134.5 ± 0.44 / 134.0–135.2	160.4 ± 0.37 / 160.0–161.0	>160.4 / 160.0–161.0

Profiles 1, 2, and 3 correspond to the treatments without fertilizers, with mineral fertilizers, and with organomineral fertilizers, respectively.

impact, humus-eluvial, dark gray, carbonate-free, loose in the upper part and compacted in the lower part, crumb structure, SiO_2 powdering, distinct transition.

A2B (35–78 cm), gray with manifested brownish tint, compacted, crumb–angular blocky structure, abundant SiO_2 powdering, clear transition.

B1 (78–133 cm), brown with pale tint, heterogeneous, well compacted, prismatic structure, mole runs, gradual transition.

B2Ck (13–159 cm), pale with brownish tint, loose, prismatic structure, wet, some calcareous inclusions, effervescence from acid, gradual transition to the parent rock.

Ck (>159 cm), parent rock, wet calcareous loess.

The description showed that no significant changes in the genetic structure of the soil occurred in the separate treatments, except the transformation of the original A1A2 horizon to the arable horizon (Table 1). The comparison of the original profile (1961) with the 2010 profile showed the migration of carbonates up the profile (Fig. 1). This phenomenon can be related to the rise of the average groundwater level during this time period. According to the initial descriptions of the soil before the establishment of the stationary field experiment, neither water nor underflooding signs were found in any profile to a depth of 2 m. At the same time, the parent rock is very wet at the depth of 170–180 cm in all three 2010 profiles, and overmoistening signs are observed below 2 m in depth. This rise of the water table, in turn, can be due to the increase in the annual precipitation, which has been observed in the last years [4, 5]. Ascending water fluxes prevailed in the lower part of the soil profile because of the shallow water depth, which favored the upward migration of calcium carbonate.

Before the beginning of the field experiment, the soil had a weakly acid reaction in the upper horizons (the pH is 5.38–5.50 in the surface layer and 5.54–5.61 in the A2B horizon), which gradually became neutral with depth.

The total acidity of the A1A2 horizon varied in the range of 2.68–2.75 meq/100 g and abruptly decreased down the profile; the degree of base saturation increased from 76.0–76.7% in the upper layer to 93–93.5%. The content of organic carbon was 1.75–

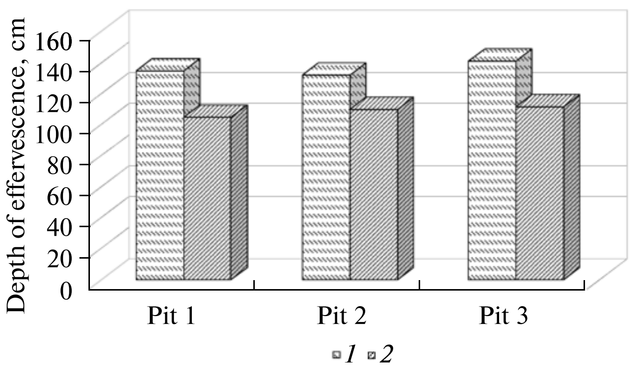

Fig. 1. Changes in the depth of the carbonate effervescence in podzolized dark gray soil from (*1*) 1961 to (*2*) 2010.

Table 2. Characterization of the original profiles (1961)

Profile	Horizon	Depth, cm	pH_{KCl}	H_{total}	Total exchangeable bases	Degree of base saturation	C_{org}
				meq/100 g soil		%	
1	A1A2	0–35	5.42	2.75	8.71	76.0	1.79
	A2B	36–70	5.54	1.25	10.89	89.7	0.71
	B1	71–130	5.73	0.68	9.70	93.5	0.48
	B2Ck	131–150	6.94	0.11	–	–	0.28
	Ck	>150	7.01	–	–	–	–
2	A1A2	0–33	5.38	2.69	8.60	76.2	1.76
	A2B	34–68	5.61	1.17	10.88	90.3	0.69
	B1	69–127	5.85	0.72	9.89	93.2	0.43
	B2Ck	128–147	7.03	0.08	–	–	0.24
	Ck	>147	7.13	–	–	–	–
3	A1A2	0–36	5.50	2.68	8.78	76.7	1.75
	A2B	37–71	5.59	1.15	10.69	90.3	0.74
	B1	72–130	5.84	0.75	9.82	92.9	0.41
	B2Ck	131–151	7.05	0.10	–	–	0.21
	Ck	>151	7.10	–	–	–	–
LSD			0.12	0.08	0.19	0.83	0.08

Here and below, a dash indicates that the parameter was not determined.

1.79% in the A1A2 horizon and also abruptly decreased with depth.

At the moment of the establishment of the long-term experiment, the spatial variation of the studied parameters among the profiles was statistically insignificant (Table 2).

In the analysis of the changes in the properties of the dark gray soil during the 1961–2010 period, the changes in the reaction of the soil solution should be noted.

In the 1961 original soil, the value of pH_{KCl} varied from 5.4 (in the upper humus horizon) to 7.0 at a depth of 2 m (Table 3). The transition from the weakly acid to the neutral reaction approximately coincided with the depth of the carbonate effervescence (120–130 cm). A tendency toward the acidification of the upper plow soil layer was observed during the entire studied period: the pH was 5.3 in 1972, 4.6 in 2001, and 4.5 in 2010. However, this tendency was valid only for the upper (0- to 30-cm) soil layer, and an inverse relationship was observed in the lower horizons. The pH_{KCl} value varied from 6.9–7.0 in the extract from the calcareous horizons (in 1961) to 7.3–7.4 (in 2010). The corresponding value for the subsurface A2B horizon also changed throughout the observation period: it increased from 5.5 to 5.8 during the first cycle of the crop rotation and varied in the range of 5.1–5.4 in the next years.

A tendency of increasing of the total acidity in the upper soil layer was also observed over the period of the studies (Fig. 2). The value of this parameter in the plow horizon increased from 2.75 (1961) to 5.59 meq/100 g soil (2010). An analogous situation could be observed in the lower carbonate-free soil layers.

The composition of the exchangeable cations in the different soil types varies in a wide range; it depends on the type of pedogenesis and the chemical composition of the soil-forming rocks and is corrected during the cultivation and active anthropogenic use. The dark gray soils of the Ukrainian forest-steppe zone are generally characterized by the high saturation of soil profile with calcium and magnesium; however, the portion of hydrogen and aluminum ions in the total exchangeable cations increases under percolative water conditions and the soil solution acidification, which is clearly demonstrated by an increase in the total acidity. At the same time, an increase in the total content of exchangeable bases, especially in the lower horizons, should be noted. This can be due to the combination of two processes: the active percolation of the soil by rain water, which favors the downward migration of carbonates, and their lifting by capillary forces due to the rise of the water table.

The rise in the total acidity and the increase in the portion of hydrogen and aluminum in the total exchangeable cations (Fig. 3) are also manifested by a decrease in the base saturation of the soil observed in the upper soil layers. The value of this parameter uniformly decreases with time from 76 to 63% in the plow horizon, from 90 to 82% in the transitional humus-

Table 3. Changes in the properties of the unfertilized dark gray soil during 1961–2010

Year	Horizon	Depth, cm	pH_{KCl}	H_{total}	Total exchangeable bases	Degree of base saturation	C_{org}
				meq/100 g soil		%	
1961	A1A2	0–35	5.42	2.75	8.71	76.0	1.79
	A2B	36–70	5.54	1.25	10.89	89.7	0.71
	B1	71–130	5.73	0.68	9.70	93.5	0.48
	B2Ck	131–150	6.94	0.11	–	–	0.28
	Ck	>150	7.01	–	–	–	–
1972	Ap	0–30	5.33	2.96	9.05	75.4	1.50
	A2B	31–62	5.81	2.12	10.10	82.7	0.88
	B1	63–105	6.14	0.96	10.70	91.8	0.29
	B2Ck	106–145	7.23	0.18	–	–	–
	Ck	>145	7.46	–	–	–	–
2001	Ap	0–32	4.61	3.39	6.20	64.7	1.53
	A2B	33–70	5.10	1.14	7.81	87.3	–
	B1	71–128	6.04	0.68	7.95	92.1	–
	B2Ck	129–150	7.02	–	–	–	–
	Ck	>150	7.21	–	–	–	–
2010	Ap	0–33	4.54	5.59	9.50	62.9	1.35
	A2B	34–72	5.43	2.39	10.97	82.1	1.22
	B1	73–130	5.67	1.43	11.03	88.5	0.45
	B2Ck	131–150	7.32	0.25	–	–	0.29
	Ck	>150	7.41	–	–	–	–

illuvial horizon, and from 93.5 to 88.5% in the B1 horizon.

The changes in the wetting, heating, and using conditions of the soils also affect the accumulation and mineralization of organic matter.

The soil organic matter is a source of plant nutrients and a factor of aggregation; at the same time, it determines the physical and physicochemical properties of the soil, including its exchange and buffer capacities, and regulates the action of excess acidity.

During the studied period, the content of organic carbon decreased from 1.8 to 1.4% in the plow horizon; its reserve in the 0- to 30-cm layer decreased from 77.8 to 58.7 t/ha, which corresponded to the loss of 9909.5 million kcal/ha. An increase in the content of carbon was observed in the subsurface A2B horizon from 0.7% at the beginning of the experiment to 1.2% in 2010 (Table 3). The total carbon reserve in the 0- to 100-cm layer did not change significantly during the period from 1961 to 2010.

The long-term cultivation and the addition of organic and mineral fertilizers significantly affect not only the nutrient status of a soil but also its physicochemical properties. As was noted above, the use of the podzolized dark gray soil most significantly affected its acidity; at the same time, differences between the experimental treatments were observed (Table 4). The values of pH_{KCl} in the plow horizon of the treatments with crop rotations and the application of mineral (profile 2) and organomineral (profile 3) fertilizers were lower than in the control (without fertilizers during the 1961–2010 period) by 5.1 and 10.2%, respectively. At the comparison of the control and the treatment with the organomineral fertilizing system, an analogous tendency could be observed for the lower layers, while the pH_{KCl} value in the treatment with mineral fertilizer was higher than in the control beginning from the subsurface horizon.

In general, for all the treatments, the reaction of the soil solution changes down the profile from weakly acid to neutral with a clear transition at the depth of carbonate effervescence. Calcium carbonates, which are lifted by capillary forces up the profile, neutralize H^+ cations, which explains the insignificant increase in pH in the lower horizons. The application of mineral fertilizers acidified the soil solution, which resulted in a decrease in the value of the parameter in the upper layers of the fertilized soils.

An analogous tendency can also be observed for the total and exchangeable acidities. Both kinds of acidity have increased values in the plow horizons and abruptly decrease down the profile in all the treat-

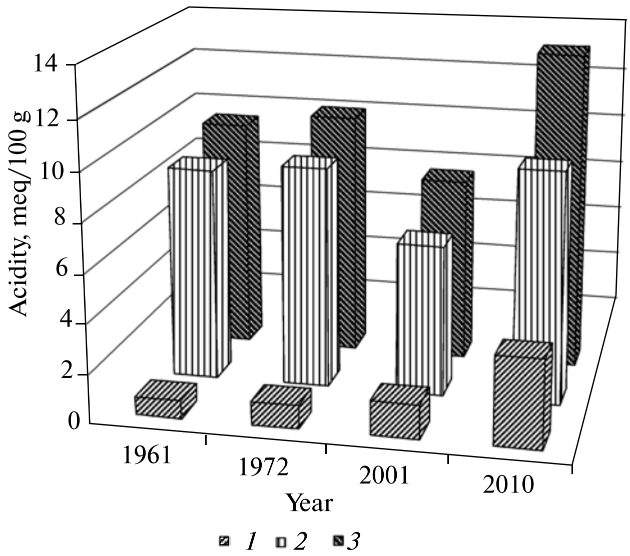

Fig. 2. Polynomial trends in changes of (*3*) the soil solution reaction and (*4*) the total acidity in the plow horizon of dark gray soils during 1961–2010: (*1*) total acidity; (*2*) pH_{KCl}.

ments. The minimum values in the plow horizons were observed in the control treatment; the application of mineral and organomineral fertilizers increased the total acidity compared to the control by 20 and 9.5%, respectively, and the exchangeable acidity by 39 and 33%, respectively. Thus, the long-term agricultural use of the soil increases its acidity, and fertilization enhances this tendency.

No significant changes were observed in the content of the total exchangeable bases in the plow horizon during the period under study; an insignificant increase in the parameter value observed in the lower layers could be due to the migration of calcium and magnesium cations.

The long-term use of the soil significantly decreased its degree of base saturation. In the plow horizon, the parameter value is in the range from 58.8 to 62.9% depending on the fertilization, while its average value was 76.5% at the moment of the establishment of the experiment; a more abrupt decrease is observed in the treatments with the application of fertilizers. At the same time, an increase in the degree of base saturation is observed in the lower soil layers in parallel with the rise of the carbonate effervescence line.

In the analysis of the evolution of the soil under the effect of long-term fertilization, special attention should be paid to the parameters of the soil humus status, because the organic substances of soils, which determine all their agrophysical, physicochemical, and biological properties, play the leading role in the development of fertility [13].

The dynamics of the organic carbon in the different treatments of the long-term experiment showed that the long-lasting use of soil largely favors its decrease in the plow layer, while the application of fertilizers partially mitigates this negative tendency. The relative decrease in the content of C_{org} in the plow horizon was 32.5% in the control and 28.7 and 19.8% in the treatments with mineral and organomineral fertilizers, respectively. At the same time, the reserves in the 0- to

Table 4. Comparative characterization of the soil profiles (2010)

Profile	Horizon	Depth, cm	pH_{KCl}/pH_{water}	H_{total}/H_{exch}, meq/100 g	Total exchange-able bases	Degree of base saturation, %	C_{org}, %
1	Ap	0–33	4.54/5.62	5.59/0.41	9.50	62.9	1.35
	A2B	34–72	5.43/6.73	2.39/0.18	10.97	82.1	1.22
	B1	73–130	5.67/7.17	1.43/0.15	11.03	88.5	0.45
	B2Ck	131–150	7.32/7.84	0.25/–	–	–	0.29
	Ck	>150	7.41/8.25	–	–	–	–
2	Ap	0–34	4.32/5.53	6.94/0.67	9.92	58.8	1.39
	A2B	35–81	6.14/7.61	1.60/0.26	11.52	87.8	1.02
	B1	82–135	6.85/7.95	0.95/0.20	11.68	92.5	0.45
	B2Ck	136–168	7.58/8.32	0.22/–	–	–	0.31
	Ck	>168	7.77/8.51	–	–	–	–
3	Ap	0–37	4.12/5.39	6.15/0.61	9.45	60.6	1.49
	A2B	38–80	5.36/6.65	1.78/0.28	10.72	85.8	1.17
	B1	81–134	5.73/6.94	1.40/0.09	11.15	88.8	0.47
	B2Ck	135–160	6.61/7.56	0.15/–	–	–	0.26
	Ck	>160	7.23/8.12	–	–	–	–
LSD			0.05/0.04	0.08/0.03	0.09	0.51	0.05

100-cm layer of the treatment with the complex fertilizing system increased by about 20 t/ha. The general increase in the water supply of the area, which could also accelerate the mineralization of organic substances, should be taken into consideration [18].

The comparison of the data on the evolution of the agrophysical and physicochemical parameters of the podzolized dark gray soils under long-term agricultural use without fertilization and at the application of mineral and organomineral fertilizers showed that this provokes agrochemical degradation in all the cases, which results in the deterioration of the suitability of the soil for intensive use. However, the degree of manifestation and evolution of the processes vary depending on the conditions. The use of soils without fertilization results in an abrupt decrease in the content of organic carbon, acidification of the soil solution, and a decrease in the degree of base saturation; under fertilization conditions, the carbon loss is lower, but the processes related to the increase in acidity and the decrease in the base saturation of the soil are enhanced.

At the same time, an abrupt decrease in the pH_{KCl} value and an increase in the total and exchangeable acidity in the upper horizons can be due to not only the anthropogenic use of soils but also due to the changes in the climatic and agroecological status of the soils in the entire zone because of an increase in the heat and water supply of the area [5]. The rise of the water table, in turn, resulted in the rise of the capillary fringe and carbonate effervescence due to the lifting of carbonates by the capillary forces. The combination of these processes explains the degradational changes in the upper horizons (decrease in pH_{KCl} and pH_{water}, increase in total acidity, decrease in base saturation) and the changes in the lower soil layers: the increase in the pH and base saturation, an insignificant increase in the cation exchange capacity, and the rise of the carbonate effervescence.

CONCLUSIONS

The study of the dark gray soil profiles in a field experiment showed that no significant changes in the genetic soil structure among the experimental treatments occurred during the period of agricultural use.

During the period of the observations (1961–2010), almost all the studied parameters of the podzolized dark gray soil were changed: the values of the pH_{KCl} and pH_{water} in the upper horizon significantly decreased; the total and exchangeable acidities increased; the degree of base saturation and the content of organic carbon decreased. In the lower horizons, the values of the pH, cation exchange capacity, and degree of base saturation increased insignificantly. The line of carbonate effervescence was lifted.

The comparative analysis of the soils occurring under different conditions of land use during 1961–2010 showed that the application of fertilizers affects the changes in the podzolized dark gray soil. Mineral fertilizers enhance the acidification of the soil solution, decrease the soil saturation with bases, but little affect the dynamics of the organic substances. The simultaneous use of mineral and organic fertilizers aggravates the above negative changes compared to the control but has a better effect than the mineral fertilizing system. The addition of organic fertilizers significantly reduces the losses of organic carbon from the plow layer and favors its insignificant accumulation in the 0- to 100-cm layer.

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