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Review article

Soil acid-base buffering in the step agriculture lands

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Modern studies of chernozem soils in the northwestern Black Sea region have shown intense dehumification due to disruption of biogeochemical cycles caused by anthropogenic removal of organic matter and associated biophile elements. At former time, the humus zoning was typical for southern chernozems and now we noted the smoothing of this zoning. Acid-base buffering has a significant role in counteracting degradation processes, the buffering parameters could be integral indicators of soil chemicals balance. We studied the automorphic soils (arable chernozems) of the northwestern Black Sea region, their humus state, particle size distribution, and acid-base buffering parameters. We studied ordinary modal and micellar-carbonate chernozems on arable land and 40-year-old fallows, southern chernozems removed from irrigation 15 years ago and southern carbonate chernozems of the second floodplain terrace of the Danube River.

We determined the neutralization index, degree of buffering capacity in the acid and alkaline ranges, equilibrium coefficient, and sodium absorption ratio to characterize the acid-base buffering. The studied soils belong to stable buffer agriculture lands by their acid-base buffer ability. We determined that soils have the parameters of chernozem type: low humus content, humate and humate-fulvate type of humus, average content of insoluble residue, high degree of humification, heavy-medium loam particle size distribution, and neutral soil solution. The acid-base buffer capacity is characterized by average values, the buffer capacity in the acid interval increases with depth, while decreases in the alkaline interval. We revealed a significant correlation between the ability to counteract the acid load and the content of physical clay. We believe that the agricultural use of southern chernozems leads to a decrease in soil resistance to acidification.

Key words: chernozems; soil organic matter; acid-base soil buffering

Introduction

Numerous studies and monitoring observations show deterioration in the fertility of chernozems when used intensively in conditions of organic fertilizer deficiency: reduction in the content of humus and plant nutrients, physical degradation, and partial loss of buffer capacity, which together testified the pronounced degradation processes in the pedosphere. In the conditions of intensification of agricultural production, the reduction of the load on the soil becomes almost impossible, so the issues of sustainability of agriculture ecosystems and soil buffering remain relevant.

Soil, due to its buffer properties, provides a balance between production and destruction of organic matter (Nadtochij et al., 2010). Soil buffering is conditioned by the ability to maintain soil component organization (Motuzova, 1994). The ability of soils to preserve genetically inherent or artificially created potentials of fertility elements and to inhibit external influences aimed at changing these potentials is defined as buffering of soil systems (Truskavec'kij, 2003). It is the acid-base buffering that is a factor in counteracting physical and chemical degradation of soils. Its parameters express the integral function of all chemical components of the soil, including products of microorganisms, as well as fertilizers, plant protection means and meliorants. Acid-base buffering is a dynamic indicator that characterizes the ability of soils to withstand pH changes with the addition of acid or alkali, and the ability to recover previous pH values (Nadtochiy, 1993, 1998). Acid-base buffer values characterize the general ecological condition of the soil and contain information on the direction and intensity of soil formation processes (Zaytseva, 1987; Sokolova et al., 1991, James, Riha, 1986; Ulrich, Pankrath, 1983; Zhang, 2016; Nelson, Su, 2010; Luo et al., 2015).

Black soils are accumulative-humus soils, they have a large area of distribution in Eurasia and North America, are characterized by a wide range of properties, have different history of land use. They are currently characterized by significant dehumification due to changes in agricultural technologies (Horáček et al., 2017, Altermann et al., 2005).

Material and methods

We studied soils within the northwestern Black Sea region. We laid down 5 key plots and 8 separate soil profiles. We studied black soils within the "Razdelnaya" site located in the South Podolsky slope and elevated area of the Dniester-Dnieper region of the northern steppe subzone of the steppe zone (Marinich et al., 2003). Geomorphological region - Dniester-Tiligul accumulative plain on Pontian basis. Common micellar-carbonate black soils differ significantly from other Ukrainian soils by their properties and regimes. We studied such soils within the key plot of "Maloyaroslavets". The site was laid within the limits of the South Moldavian slope and elevated area of the Dniester-Dnieper region of the north-steppe subzone of the steppe zone. Geomorphological region - Kogilnitskaya erosion-denudation loess plain. We analyzed the southern black soils within the key plot "Molodezhnoye". The site is situated within the Dniester-Bug lowland region of the Black Sea region of the steppe subzone of the steppe zone, in the lowland coastal plain of the Upper Pliocene undivided terraces. We studied soils in the arable and 40-year-old fallow areas to analyze the evolution of buffer capacity parameters. The key plot "Glubokoye" is located on the territory of the Zadnestrovsko-Prichernomorskaya lowland region of the Black Sea region of the middle-steppe subzone of the steppe zone. In this area we studied the peculiarities of the southern chernozems, which were removed from the irrigation 15 years ago. The plot is a lowland coastal plain of Upper Pliocene undivided terraces. The study of the southern carbonate black soils in Lower Danube floodplain terraces was carried out within the limits of the "Izmail" plot. According to the physical and geographical zoning the site is located in the Zadnistrovsko-Prichernomorskaya lowland area of the Black Sea region of the middle steppe subzones of the steppe zone. Geomorphologically, the area is a terrace plain of the Danube River.

We studied the morphological properties of soils in the main and auxiliary soil profiles. For laboratory and analytical studies, the soil samples were taken in layers, taking into account genetic horizons. We used National Standards and other methods for soil testing. In the selected soil samples we determined acid-base buffer properties by potentiometric method (DSTU ISO 10390-2001), the sodium resistance by V.P. Bobkov method (Motuzova, Bezuglova, 2007); organic matter we determined by GOST 4289-2004; we determined humus group and particle composition by N.N. Kononova and N.P. Belchikova (Kononova, Belchikova, 1961, Kononova, 1963); we used pipette method in modification of N.A. Kachinsky for particle size distribution by (DSTU 4730-2007).

To assess the humus state of soils D.S. Orlov and L.A. Grishina developed a system of assessment of the level and state of humus based on the chemical distribution of organic matter. This system allows to estimate the direction and rates of humification, provision of soils with humus and nitrogen, as well as the quality of humus. One of the important indicators of this system is the content of humus in the accumulative horizon, and for cultivated soils - in the arable layer.

Results

We characterize the studied ordinary chernozems as low humus in terms of humus content in the arable layer (3.6-3.8%). As we move southward, the continental climate increases and we registered less favorable conditions for the accumulation of organic matter. We marked out the southern black soils as weak humus soils; they have a humus content of 2.2-2.6%. We note the lack of clear differentiation between ordinary and southern black soils in terms of humus content, which was reported at the beginning of the XX century by A.G. Nabokikh (Nabokikh, 1915), which indicates the leveling of humus zoning. At the same time, the geographical distribution of humus is preserved, namely the reduction of its content and layer thickness from the north to the south (Table 1).

The group composition of humus is characterized by a relatively high amount of humic acids and a relatively small amount of fulvic acids, which is typical for soils of chernozem type. We found that the relative content of humic acids in the arable layer of chernozems of common and southern areas under study ranges from 26 to 40%. The lowest content of humic acids is noted in the chernozems of southern carbonate Lower Danube floodplain terraces, the middle loam composition of which determines the low absorbing capacity, which is a prerequisite for the consolidation of newly created humus substances. A sharp decline in humic acids is also associated with a decrease in the solubility of humus: the yield of humus solution is 41-49%. The greatness of the output of humic substances in the solution at their fractionation is influenced by the content of calcium carbonate in the soil. Soil carbonation reduces the solubility of humus, despite the fact that carbonates decompose and completely wash out Ca with soil lot during decalcification.

The ratio of humic acids and fulvic acids characterizes the type of humus and reflects the specificity of humification in different soils. The studied chernozems have humate-fulvate type of humus in the arable layer at a ratio of C_h:C_f within the limits of 1.76-1.84. In the subpathobic layer there is an increase in the relative content of humic acids and the expansion of C_h:C_f to 2.02-2.21, which is typical for a humane type of humus. For the southern chernozems, a gradual decrease in the relative and absolute content of humic acids down the profile is typical and, accordingly, a narrowing of the ratio of C_h:C_f with depth. The humus accumulative horizon of the southern chernozems is characterized by a humane type of humus on an arable land (C_h:C_f ~ 2.27) and on 40-year-old fallow (C_h:C_f ~ 2.0-2.6). The southern black soils, excluded from irrigation, and the southern carbonate black soils of the Lower Danube Floodplain Terrace have a humate-fulvate type of humus with a ratio of Sgc: SFC in the range of 1.75-1.87, which gradually decreases down the profile. The relative content of insoluble residue in ordinary and southern black soils varies between 42-59%. Most fully organic residues are converted into humic substances in common chernozems, as evidenced by a high degree of humification (31.0-38.5%) in the humic part of the profile. The degree of humification of the southern chernozems in the upper layer is high (36.2-40.0%), this indicator decreases with the depth up to 22.0-26.3%. The exception is the south carbonate black soils of Lower Danube floodplain terraces, which are characterized by an average degree of humification, and beginning with a depth of 24 cm – by weak (10.7-19.5%).

Table 1. Humus state of automorphic soils

Depth, cm	Organic matter, %	$Na_4P_2O_7$+NaOH extractable orgamic matter		C_h, %		C_f, %		C_h.:C_fr ratio	Insoluble residues, %		Humification, %
		1	2	1	2	1	2		1	2	
Southern carbonated chernozem, medium humified, low-humic, middle loamy, arable (Izmayl Plot)											
0-11	2.16	0.52	41.3	0.34	26.9	0.18	14.4	1.87	0.73	58.7	26.9
11-24	2.03	0.55	46.8	0.34	28.5	0.22	18.3	1.56	0.63	53.2	28.5
24-37	2.12	0.61	49.8	0.24	19.5	0.37	30.2	0.65	0.62	50.2	19.5
southern chernozem, medium humified, low-humic, middle loamy, arable (Molodizhme Plot)											
0-4	2.62	0.88	57.6	0.61	40.0	0.27	17.6	2.27	0.64	42.4	40.0
4-34	2.90	0.91	54.3	0.62	37.1	0.29	17.2	2.16	0.77	45.7	37.1
34-47	2.81	0.79	48.3	0.42	25.6	0.37	22.7	1.13	0.84	51.7	25.6
southern chernozem, low-humic, fallow (Molodizhne Plot)											
0-10	4.16	1.15	47.8	0.83	34.5	0.32	13.3	2.60	1.26	52.2	34.5
10-20	3.73	1.08	50.0	0.72	33.3	0.36	16.7	2.00	1.08	50.0	33.3
20-30	3.63	0.85	40.4	0.52	24.7	0.33	15.8	1.57	1.26	59.6	24.7
southern chernozem, medium humified, low-humic, heavy loamy, post-irrigated, arable (Glyboke Plot)											
0-10	2.43	0.80	57.0	0.51	36.2	0.29	20.8	1.74	0.61	43.0	36.2
10-20	2.57	0.82	55.3	0.52	34.9	0.30	20.4	1.71	0.67	44.7	34.9
20-30	2.40	0.85	61.3	0.51	36.8	0.34	24.5	1.51	0.54	38.7	36.8
regular micellar-carbonated chernozem, heavy loamy, low-humic, arable (Maloyaroslavets Plot)											
0-15	3.64	0.86	40.9	0.56	26.5	0.30	14.4	1.84	1.25	59.1	26.5
15-25	3.34	0.91	46.9	0.62	31.7	0.29	15.2	2.09	1.03	53.1	31.7
25-35	3.29	0.90	47.1	0.61	31.7	0.30	15.4	2.05	1.01	52.9	31.7
35-45	3.3	0.94	49.0	0.63	33.1	0.30	15.9	2.08	0.97	51.0	33.1
45-55	3.1	0.98	54.3	0.66	36.4	0.32	17.9	2.03	0.82	45.7	36.4
regular zhernozem, medium humified, low-humic, heavy loamy, arable, (Rozdilne Plot)											
0-10	3.86	1.09	48.8	0.70	31.1	0.40	17.7	1.76	1.15	51.3	31.1
10-20	3.59	1.16	56.0	0.80	38.5	0.36	17.4	2.21	0.92	44.0	38.5
20-30	3.65	1.15	54.3	0.77	36.5	0.38	17.9	2.04	0.97	45.7	36.5
30-40	3.6	1.01	48.7	0.68	32.7	0.33	16.0	2.04	1.06	51.3	32.7
40-56	3.1	0.80	52.9	0.53	35.4	0.27	17.6	2.02	0.71	47.1	35.4

Note: 1 – as a percentage of the soil weight, 2 – a percentage of organic matter. C_h – humic acid contamincation, C_f - fulvic acid comntamination.

According to the data of B.S. Nosko, the return of black soils into the fallow causes humus formation regimes typical for virgin chernozems for 45-50 years (Nosko, 2006). Our comparative studies of the southern chernozems in the 40-year-old fallow and arable land showed that intensive agricultural use is accompanied by noticeable changes in the group composition of humus. We note a 16 % increase in the relative content of humic acids, a 32 % increase in fulvic acid content, and a 19 % decrease in the insoluble residue content. We have revealed a tendency to increase the solubility of humic substances by reducing the strength of their bonds with the mineral part of the soil. We registered some features of granulometric composition of soils (Table 2). Normal and conventional micellar-carbonate black soils are classified as coarsely dispersed-silty heavy loams (48-52% of physical clay (PC) content). The prevailing fractions for the whole profile of common chernozems are dust (particles smaller than 0.001 mm) and coarse particles (0.05-0.01 mm). We observed a lower content of physical clay (about 46%) in the southern, irrigated black soil, which characterizes them as heavy loam. Southern black soils and southern carbonate black soils of the Lower Danube floodplain terraces have a medium loamy granulometric composition (35-42% of physical clay). In contrast to conventional black soils, the predominance of the coarse particle fraction in the entire profile is characteristic of the southern soils with a slightly lower silt fraction. The exception is the southern carbonate black soils, for which fine sand (0.25-0.05 mm) is the second predominant fraction.

In 25 % of all investigated soils the content of sand fraction fluctuates within the limits of 1.0-0.05 mm that testifies to equal composition of soil-forming rocks. We noted a small content of coarse and medium sand fraction (1-0.25 mm) in 1% of the studied chernozems, which negatively affects the physical properties of the soil, causing soil overcrust and soil cap after precipitation. Medvedev and Laktionova claim that the content of fine particles and sand fraction is inherited from the mother rock (Medvedev, Laktionova, 2011). They also note the existence of zonal differentiation in the grain size distribution of soils.

For the steppe zone, the dust is the predominant fraction, which is confirmed by our studies. We noted the highest content of dust fraction (about 55 %) for the black soils of the southern carbonate Lower Danube floodplain terraces, and for the upland of the southern black soils (47-50%). Common black soils contain about 42-44 % of the dust fraction. We registered the content of fine and medium dust (0.005-0.001 mm and 0.01-0.005 mm) in 15-20 % of all studied soils and this promotes siltation and deflation processes. Mud actively participates in the processes of soil formation and migration of substances, which determines the diversity of its content in soils. Thus, the southern carbonate black soils of the Lower Danube floodplain terraces in the arable layer of soil contain the smallest amount of mud fraction (about 20%), the southern black upland soils - 26-28%. Normal black soils have the highest mud content (32%), which ensures their high absorption capacity.

Table 2. Granulometric composition of soils

Depth, cm	Hygroscopic moisture, %	Particle size (mm) and contamination (%)						Particle share, less than 0.01mm %	Soil granulometric type
		Physical sand			Physical loam				
		Sand		Dust			Mud		
		1-0.25мм	0.25-0.05	0.05-0.01	0.01-0.005	0.005-0.001	<0.001		
1	2	3	4	5	6	7	8	9	11
Southern carbonate chernozem									
0-11	2.79	0.38	24.53	39.36	6.63	9.95	19.15	35.73	Middle loamy
11-24	2.77	0.28	25.30	38.79	5.05	10.61	19.97	35.63	Middle loamy
24-37	2.76	0.26	25.81	37.73	4.49	13.12	18.59	36.20	Middle loamy
Southern arable chernozem									
0-4	3.23	0.19	22.46	35.03	7.21	8.55	26.56	42.32	Middle loamy
4-34	3.86	0.32	21.76	34.09	6.09	10.96	26.78	43.84	Middle loamy
34-47	3.86	0.27	22.45	34.03	5.82	11.54	25.89	43.25	Middle loamy
Southern post-irrigated chernozem									
0-10	4.28	0.26	23.22	30.20	7.95	9.57	28.80	46.31	Heavy loamy
10-20	3.90	0.25	22.61	30.41	8.05	9.88	28.80	46.73	Heavy loamy
20-30	4.30	0.28	21.68	32.46	6.09	10.21	29.28	45.58	Heavy loamy
Regular micellar-carbonated chernozem									
0-15	4.73	1.25	23.80	26.45	4.75	11.42	32.33	48.50	Heavy loamy
15-25	4.76	1.41	24.37	27.48	5.17	10.42	31.15	46.74	Heavy loamy
25-35	5.21	1.05	29.03	21.32	4.93	9.51	34.16	48.60	Heavy loamy
35-45	4.90	1.26	27.12	22.34	5.40	10.92	32.96	49.28	Heavy loamy
45-55	4.31	0.90	25.76	22.16	7.20	12.98	31.00	51.18	
Regular chernozem									
0-10	5.17	0.44	23.69	23.80	7.56	13.06	31.45	52.07	Heavy loamy
10-20	4.98	0.45	25.01	22.01	7.92	12.03	32.58	52.53	Heavy loamy
20-30	5.30	0.26	25.22	27.17	7.29	12.79	27.27	47.34	Heavy loamy
30-40	5.62	0.45	19.29	27.27	6.25	12.19	34.55	52.99	Heavy loamy
40-56	5.27	0.30	24.22	25.05	6.15	11.80	32.48	50.43	Heavy loamy

Soils profile differentiation by their granulometric composition depends on their silt content and finer fractions. The more fine particles in the soil, the greater the possibility of their migration along the profile. Active soil-forming processes (salinization), which lead to dispersion of finely dispersed mass, and the presence of porous space, which causes its movement along the profile, also play an important role. Granulometric profile of the southern black soils and black conventional micellar-carbonate soils is characterized by weak differentiation of silt. We registered a growth of silt fraction with depth in the black southern carbonate soils of Lower Danube floodplain terraces and ordinary black soils.

Acid-main buffering of black soils. The studied soils are characterized by neutral and slightly alkaline reaction (pH 6.45-8.50, see Table 3). For all the soils, there is an increase in pH downwards in the profile, which is associated with an increase in the content of calcium and magnesium carbonates in the lower horizons. Soil solution reaction is closely connected with soil composition, character of its use and direction of soil formation. Most of the processes in the soil occur with the release or absorption of protons, which forms the acid-base buffer of the soil. Its effectiveness explained the ability of soils to dampen the high amplitude of proton activity in the reactions, which are expressed in the scheme of acid = base + proton.

Processes involving protons are associated with carbon, nitrogen, sulfur, and some trace elements, as well as with the migration of alkali and alkali-earth metals in the soil profile (Nadtochij et al., 2010). B. Ulrich developed the concept of buffer systems, which reflects the different behavior of soil buffer mechanisms depending on the genetically inherent pH value (Ulrich and Pankrath, 1983). We studied the soils are characterized by a coal buffer system, in which carbonates are the main substances responsible for creating the buffer. The eluvial crust on the surface of the studied common and southern chernozems with pH < 6.2 is characterized by a silicate buffer system. The main buffer mechanism of this system is the weathering of silicates (Truskavec'kij, 2003). Based on the analysis of literature and our own observations, we concluded that it is possible to use the parameters of acid-base soil buffering to assess the agricultural and ecological condition of soils. These are the neutralizing index (NI), the degree of buffering in acid and alkaline intervals (BD_{HCl} and BD_{NaOH}), and the index of acid-base equilibrium ($I_{ab} = BD_{HCl} / BD_{NaOH}$). When the buffer capacity index is used to assess soil buffer properties, the buffer capacity area loses its meaning and should be used for intermediate calculations (Truskavec'kij, 2003).

The neutralizing capacity of the soil is expressed through a neutralizing index (NI) that corresponds to the milli-equivalents (meq) of acid or alkali per 100 grams of soil that provides a neutral reaction (Nadtochij et al., 2010). In the upper horizons of the studied soils the alkaline pH ranges from 1.25-5.5 meq / 100 g, and in the lower horizons acid pH - 0.75-1.25 meq / 100 g. In chernozems of southern carbonate the index of neutralization in the acid interval reaches 12.0 meq / 100 g.

Table 3. Buffer capacity of automorphic soils

Plot and soil type	Depth, cm	pH	Buffering area, cm^2		Neutralizing index, meq/100 g		Buffering capacity, %		BD_{HCl}: BD_{NaOH} ratio
			Acid range	Alki range	Acid range	Alki range	Acid range	Alki range	
Souther carbonate chernozem (arable)	0-11	7.15	23.66	9.63	1.25	-	87.4	37.7	2.3
	11-24	8.35	26.61	9.65	5.75	-	80.5	49.3	1.6
	24-37	8.50	27.50	9.13	12.0	-	85.1	44.9	1.9
Southern chernozem (fallow)	0-4	5.70	10.16	14.80	-	5.5	51.3	53.6	1.0
	4-34	6.85	13.17	15.51	-	0.5	51.5	58.6	0.9
	34-47	7.65	15.76	11.77	1.25	-	53.3	45.9	1.2
Southern chernozem (fallow)	0-10	6.45	15.00	13.75	-	2.0	63.6	51.2	1.2
	10-20	6.50	14.74	13.56	-	0.75	56.8	56.2	1.0
	20-30	7.64	14.41	10.78	0.75	-	46.5	60.1	0.8
Southern chernozem (post-irrigated	0-10	6.40	12.59	12.21	-	1.25	54.0	45.4	1.2
	10-27	7.48	15.53	13.14	0.7	-	54.1	50.8	1.1
	27-44	7.70	16.67	9.19	1.25	-	55.9	35.9	1.6
Regular micellar-carbonated chernozem	0-15	6.60	13.50	13.26	-	1.25	55.5	49.6	1.1
	15-35	7.10	14.74	13.56	-	0.2	54.9	51.7	1.1
	35-55	7.38	14.41	10.78	0.75	-	51.1	41.6	1.2
Regular chernozem	0-10	5.66	11.76	16.19	-	5.0	59.9	58.5	1.0
	10-34	6.85	14.45	14.53	-	0.5	56.5	54.9	1.0
	34-56	7.28	15.74	11.93	0.75	-	56.8	45.9	1.2

Note: BD_{HCl} - degree of buffer capacity in the acidic interval; BD_{NaOH} - degree of buffer capacity in the alkaline interval.

Another indicator characterizing the acid-base buffering of the soil is the buffer area, which is 10.2-16.7 cm^2 in the studied soils. The buffer capacity of the soil profiles analysed was assessed based on the area of buffer surfaces in acidic (P_{HCl}) and alkaline (P_{NaOH}) range, drawn for soil samples taken from individual genetic horizons. The buffer area in the acid interval of soils under study with depth increases, and in the alkaline interval - decreases. This is explained by partial migration of the highly buffer colloidal fraction of the organic-mineral complex with respect to acids to the lower horizons (Nadtochiy, 1993). The largest buffer area (23.7-27.5 cm^2) against acidification have carbonate soils of the Lower Danube floodplain terraces with relatively light granulometric composition. Such soils have the lowest value of 9.1-9.6 cm^2 in the alkaline interval.

Analyzing the anthropogenic impact on the acid-base buffer properties of soils, it is necessary to note a 33% decrease in the buffer area in the acid interval and a 7% increase in the alkaline area in the arable layers of chernozems of the southern arable lands, as compared with chernozems log. The degree of buffer capacity makes it possible to assess the soil buffer capacity in the same pH ranges relative to the absolute buffer standard, the pH of which corresponds to the sample under study (Nadtochij et al., 2010). On the basis of the acid-base soil buffer assessment scale, the studied black soils are estimated to have an average degree of buffer capacity within the acidic interval (buffer capacity 60%). The exception is the black earths of the southern carbonate Lower Danube floodplain terraces, which are characterized by a very high buffer capacity in this range (80-87 %). High alkaline buffering capacity is observed in common and southern black soils - 53-58%; other studied soils are characterized by an average buffer in the alkaline interval - 38-51%. The parameters of soil buffer capacity assessment objectively reflect the changes occurring under anthropogenic impact. As a result of agricultural use of the southern chernozems, a decrease in the degree of buffer capacity in the acidic interval and its increase in the alkaline range are observed.

An additional criterion for assessing the stability of the functioning of agro-ecosystems is the index of acid-base equilibrium, $I = BD_{HCl} / BD_{NaOH}$, (Nadtochiy, 1998). According to this indicator, the studied black soils are more stable than the southern carbonate soils (I = 1.0-1.2 and 2.3, respectively). Climatic conditions, specific water-thermal and biological regimes of soils, which determine the high mobility of carbonates within the soil profile on relatively light soils with respect to particle size distribution, reduce the stability of acid-base equilibrium. Soil systems function in a relatively ecologically sustainable regime, with $BD_{HCl} + BD_{NaOH}$ exceeding 70-75% and BD_{HCl} / BD_{NaOH} varying between 0.6-4.0 (Nadtochij et al., 2010). Soil studies on these indicators are characterized as ecologically stable soil systems. The processes of formation of black soil of the southern withdrawn from treatment are characterized by reduction of pH of water suspension, reduction of neutralization index (IN → 0) and leveling of buffer capacity in both intervals (Kr → 1), the total buffer capacity increases ($BD_{HCl} + BD_{NaOH} \rightarrow 200\%$). As noted by P.P. Nadtochiy, the formation of such conditions without anthropogenic removal of organic matter and associated biofilm elements contributes to the manifestation of the principle of almost complete closure of biogeochemical cycles in these ecosystems of the biosphere (local landscapes).

The leading factor in the formation of alkaline soil environment in the steppe zone is the processes of sodogenesis, which are counteracted by pH-buffering. It is known that sodium soda has a toxic effect on the growth and development of cultivated plants and the appearance of soda in soil solution as the most toxic among other water-soluble mineral salts can lead to complete plant death. Soil co-neutralizing function of soils (pH-buffering) is their ability to counteract the processes of sodogenesis in soil solution (Truskavec'kij, 2003). The sodium resistance (sodium hypofertness), i.e. the amount of sodium that can neutralize the soil, in the studied chernozems of the south ranges from 23.7 to 30.0 meq / 100 g (Table 4).

Table 4. Sodium resistance of automorphic soils, meq /100 g.

Soil horizon	Type of chernozem					
	South carbonated	Southern, arable	Southern, fallow	Souther, post-irrigated	Regular micellar-carbonated	Regular
Ha	26.7	30.1	25.4	28.1	28.8	32.4
H	25.3	26.3		30.0	34.6	36.6
Hp	23.7	27.7	No data	29.2	34.2	36.8

For regular chernozems, the sodium resistance index is slightly higher and reaches 36.8 meq / 100 g. According to V.P. Bobkov's classification, all studied soils have a low degree of sod resistance (20-35 meq / 100 g) (Motuzova and Bezuglova, 2007).

Relationship of acid-base buffer parameters to soil composition. Analyzing the obtained data, the dependence of the parameters of acid-base buffering on the granulometric composition and humus state of soils was noted. For more accurate conclusions, the graphical analysis was carried out, the result of which is shown in Fig. 1. The dependence between the degree of buffer capacity in the acid interval and the content of mud fraction (Fig. 1.1), as well as the content of physical clay (Fig. 1.9) was analyzed.

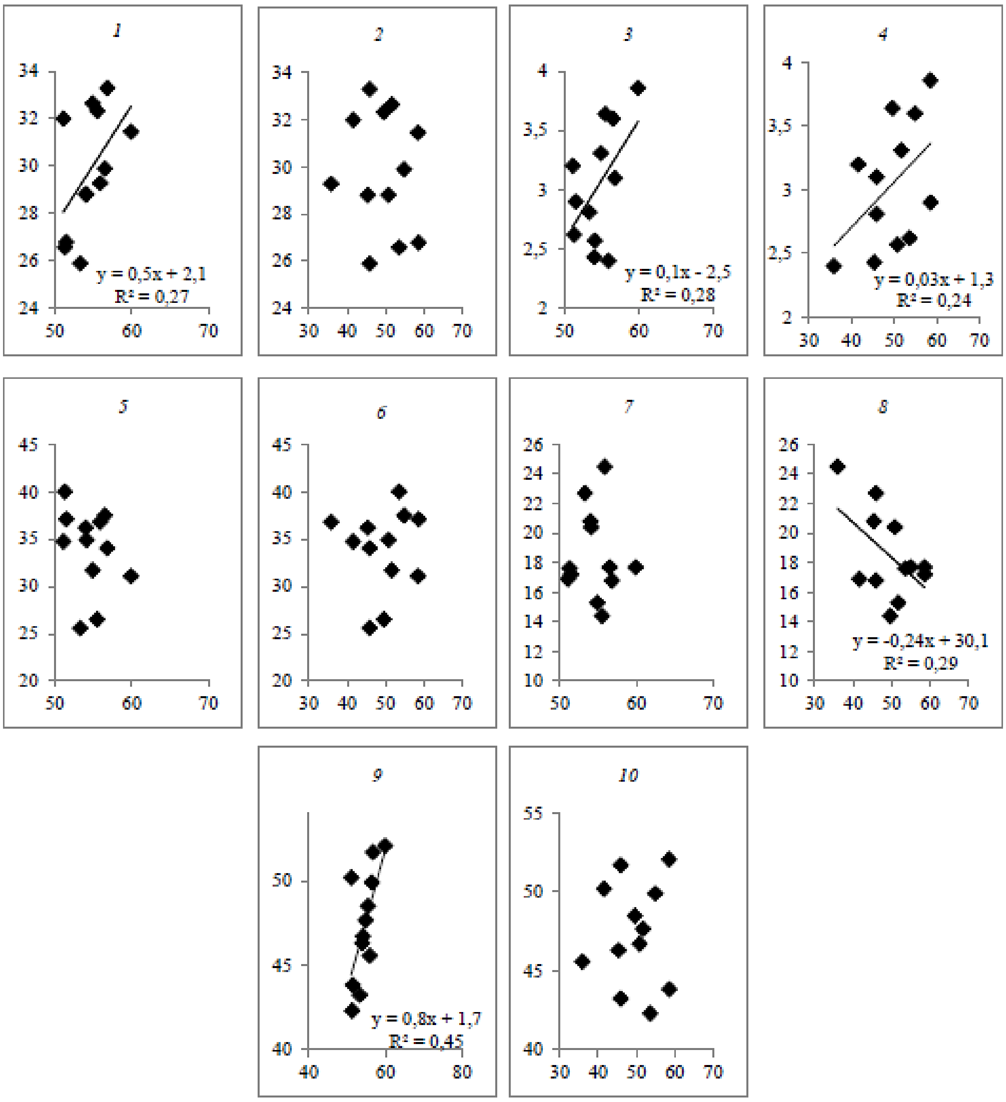

Fig. 1. Relationship of acid-base buffer parameters with soil composition: 1 - acid-base buffer capacity in the acid interval and mud content (here and furtner all values are in %); 2 - acid-base buffer capacity in the alkaline interval and mud content; 3 - acid-base buffer capacity in the acid interval and humus content; 4 - acid-base buffer capacity in alkaline interval and humus content; 5 - acid-base buffer capacity in acid interval and humic acid content; 6 - acid-base buffer capacity in alkaline interval and humic acids content; 7 - acid-base buffer capacity in acid interval and fulvic acids content; 8 - acid-base buffer capacity in alkaline interval and fulvic acids content; 9 - acid-base buffer capacity in the acidic interval and physical clay content; 10 - acid-base buffer capacity in the alkaline interval and physical clay content.

According to the results of statistical analysis, the average positive correlation (r = 0.52 and r = 0.67, respectively) was established. According to the determination coefficient, 45% of the changes can be explained by the content of physical clay. The correlation between the degree of buffer capacity in the acid interval and the content of physical clay is significant, which allows to reject the null hypothesis at 5% level. The buffer capacity in the alkaline interval has a weak insignificant dependence on the content of silt (Fig. 1.2) and physical clay (Fig. 1.10); the correlation coefficient does not exceed the value of 0.3. Some authors noted the dependence between silt content and soil buffer capacity (Nadtochij, et al., 2010; Gamkalo, 2002), but for the studied black soils the dependence is insignificant, which is subject to the genesis homogeneity of granulometric fractions and their subsequent evolution.

Conclusions

We characterized the chernozems of arid steppes as stable buffer agricultural systems under intensive agricultural use and deficiency of organic substances on parameters of acid-base buffer ability. Such chernozems have the humus content of 2.2-3.8%, humane and fulvate-humane type of humus, moderate content of insoluble residue, a high degree of humification, heavy and medium loam granulometric composition, mainly neutral reaction of soil solution. Their acid-base buffer capacity is characterized by average values, the buffer capacity increases in the acid interval with soil depth, and decreases in alkaline range.

The aridization and decreasing of humus decline the soil resistance to the ecologically dangerous sodicity, which is typical for a steppe zone. Geomorphological and climatic conditions influence not only zonal regularities of soil formation, but they also form the facial features of soils. Thus, ordinary micellar-carbonate black soils have a relatively powerful humus part of soil profile, and high mobility of carbonates in their profiles that causes weakening of the alkali neutralization capacity.

Parameters of soil acid-base buffering reflect local peculiarities of soil condition. Average loamy soils are characterized by relatively high capacity in acidic range and the lowest capacity in alkaline interval. They have almost zero neutralization index in alkaline interval. According to the index of acid-base equilibrium, these soils are characterized as insignificant ecologically stable agricultural systems, which are subject of their qualitative state and resistance to physical and chemical degradation. Intensive agricultural use of chernozems in arid conditions leads to reduced resistance of soils to acidification, growth of alkaline loads and weakening of sodium neutralizing capacity. Southern black soils excluded from irrigation are defined as insignificant stable agricultural ecosystems according to the index of acid-base equilibrium in the sub-arable horizons.

We revealed the moderate correlation between the degree of buffer capacity in the acidic interval and the content of humus, silt and physical clay. We also observed moderate correlation between the ability to counteract alkaline loading and the content of humus and fulvic acids. Thus, the index of neutralization, the degree of buffer capacity and the index of acid-base equilibrium of chernozem soils is an objective criterion of the quality of the soil system reflect the nature of anthropogenic impact and peculiarities of soil-forming processes.

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