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SOME PHYSICOCHEMICAL PROPERTIES OF PHAEOZEMS IN BULGARIA

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Abstract

The main components of the cation exchange capacity (CEC) are assessed in order to study the physicochemical properties in Phaeozems. These soils in Bulgaria usually have high humus accumulation, soil texture differentiation, high base saturation and soil reaction suitable for crops. They are spread in plains, valleys, forests and low hills with temperate continental climate. Soil-forming materials are Pliocene and Quaternary sediments, loess and loess-like clays. The soil reaction (pH) varies from slightly acidic to alkaline. Soil alkalinity increases in depth because of high carbonate mineral compounds that mainly contain Ca and Mg. Total acidity and exchange acidity are in very low values. Exchangeable Ca consists about 78 % of CEC. It is established that soil colloids are occupied by Ca and Mg ions, which determined the stability of clay minerals. Phaeozems have favorable physicochemical properties with high cation exchange capacity and base saturation. These soils are highly valued for their fertility potential.

Key words: base saturation, CEC, soil reaction, total acidity.

Introductions

According to WRB (IUSS Working Group WRB 2015), Phaeozems cover an estimated 190 million hectares world-wide. Some 70 million hectares of Phaeozems are found in the USA, in the sub-humid central lowlands and parts of the Great Plains. Fifty million hectares of Phaeozems are in the subtropical areas of South America and the third largest distribution area of Phaeozems (18 million hectares) is in Northeastern China. Smaller, mostly discontinuous areas are in Central Europe, notably in Danube region of Hungary, Serbia, Romania and Bulgaria.

Phaeozems are widespread between Chernozems and ordinary loess soils in areas with temperate continental climate in Northern Bulgaria. The relief on which they are located is flat and slightly hilly. Soil-forming materials are loess and loess-like clays. In Southern Bulgaria they are usually spread over different Quaternary materials. In the past most of these soils were under forest but now they are fertile and arable lands (Ninov 2002, Teoharov 2019)

In Bulgaria Phaeozems are characterized by thick surface horizon (A) of 30–40 cm and up to 80–120 cm Bt horizon, respectively, with fine granular (irregular) to small prismatic and large granular structure. These soils have a dark gray surface and a dark gray or dark brown luvic-metamorphic (cambic) horizon, with low textural differentiation. The base saturation throughout the profile is 70–90 %, the soil reaction is slightly acidic to medium acidic in the surface. The cation exchange capacity in A horizon ranges from 17–27 to 36 meq/100 g soil, and in Bt horizon from 14 to 31 meq/100 g soil. The soil texture could be loamy-clay, sandy-clayey and rarely clayey with a distinct process of *in situ* clay formation and a gradual decrease in humus (Ganev and Arsova 1980, Malinova 2010, Shishkov and Kolev 2014, Nikova et al. 2017).

According to Habel et al. (2007), Phaeozems have neutral reaction because of the presence in the parent material with different quantities of natural calcium carbonate. This confirms considerable buffer capacity and high 'natural 'resistance of these soils to degradation processes. A very high degree of base saturation should be assessed as exceptionally favourable for the growth and development of crop plants.

Phaeozems usually have neutral soil reaction at the surface. The optimum range for most agricultural crops is between 5.5 and 7.5, $pH_{(H2O)}$ and the most of nutrients are available. Soil alkalinity increases with weathering of silicate, aluminosilicate and carbonate mineral compounds that contain Na, Ca, Mg, NH_4 and K. The fore-listed minerals are usually added to the soil by the deposition of eroded sediments by water or wind (Oshunsanya 2018).

Similar research of effective cation-exchange capacity by low values is found in Romania (from 14.57 to 19.82 meq/100 g soil), and the degree of base saturation in surface horizon is (67.8 %), decreases abruptly (42.1 %) in deeper layers (Stanila et al. 2017, Stanila 2019). Researches about Phaeozems are made also in Eastern Qinghai-Tibet (Ma et al. 2020). The soils are similar with thick, dark-coloured surface horizon with high base saturation and a moderate to high content of organic matter.

The aim of this study is to determine main physicochemical indices of Phaeozems such as ability of soil to adsorb cations in exchangeable forms and to establish buffer capacity of soil. Some relationship would therefore be expected between soil pH, CEC and of base saturation.

Material and Methods

The main diagnostic soil characteristics were obtained using the following methods: soil pH was measured in water suspension 1:2.5. The exchangeable Al was determined titrimetrically after displacement of Al ions by 1 N $CaCl_2$. The total exchangeable hydrogen exch. $H_{8.2}$ (total acidity) and exchangeable bases (Ca and Mg) were determined titrimetrically and complexometrically, respectively, after saturation of the soil sample with buffer solution (Na-acetate and K-maleate, $pH_{(H2O)}$ = 8.2). CEC was calculated by the sum of $H_{8.2}$ and exchangeable bases in meq/100 g – method of Ganev and Arsova (1980). Base saturation is the percentage of CEC that is saturated with base exchangeable cations (Ca and Mg). It is calculated according to this formula (1).

$$V\% = 100 \times \frac{\sum sum}{CEC}, \tag{1}$$

where: $V\%$ is base saturation, Σsum is the sum of exchangeable cations, CEC is the cation exchange capacity of the soil in meq/100 g. CEC is conventionally expressed in meq/100 g (Rengasamy and Churchman 1999) which is numerically equal to centimoles of charge per kilogram of exchanger (cmol(+)/kg).

For statistical analyses and graphics was used Microsoft Excel 2010 software. Six soil profiles are presented, one of them is from South Bulgaria – profile one (P1) close to Novi Han village, Sofia district. The rest of the soil profiles are from northern part of Bulgaria – profile 2 (P2) Volovo village, Rousse district; profile 3 (P3) Bezhanovo village, Lovech district; profile 4 (P4) Voidiza village, Turgovishte district; profile 5 (P5) Vladimirovtzi village, Razgrad district; profile 6 (P6) town of Isperih, Razgrad district. For soil profiles 3, 4, 5 and 6 the values are taken from Ganev et al. (1990).

Results

The obtained results show that Phaeozems are rich in bases in deep of the soil profile (Table 1). They have dark coloured surface horizon (figs 1 and 2) with favourable soil reaction. These soils are from neutral to moderately acidic $pH_{(H2O)}$ in surface horizon A (5.3–6.7) to medium alkaline reaction only in Ck (7.7–8.2). The mean value of soil pH is 6.55, which is favourable soil reaction for main crops (tables 1 and 2).

Table 1. Soil profiles with physicochemical properties.

Horizon/ Depth, cm	$pH_{(H2O)}$	CEC	ex. $H_{8.2}$	ex. Al	ex. Ca	ex. Mg	*V*, %
		meq/100 g soil					
			P1. Endocalcic Luvic Phaeozem				
Ap 0–24	5.5	37.5	11.0	0.9	23.0	3.2	70.67
Bt1 2–49	6.0	43.5	7.1	0.0	33.0	3.4	83.68
Bt2 49–67	6.5	43.4	5.2	0.0	34.8	3.4	88.02
Ck1 67–95	7.5	34.9	0.0	0.0	31.6	3.3	100
Ck2 95–150	7.7	38.0	0.0	0.0	34.5	3.5	100
			P2. Bhatycalcaric Luvic Phaeozem				
Ah 0–18	6.7	30.6	3.8	0.0	24.0	3.0	87.58
A2 18–40	6.8	30.0	3.5	0.0	23.2	3.0	87.33
AB 40–75	6.8	27.7	2.5	0.0	23.0	2.5	90.67
Bt1 75–108	6.8	31.0	1.6	0.0	27.0	2.4	94.84
Bt2 108–139	7.0	25.8	1.6	0.0	21.2	2.8	93.80
Ck1 139–160	8.1	25.0	0.0	0.0	22.0	3.0	100.00
			P3. Endocalcic Luvic Phaeozem				
Ap 0–29	6.3	33.6	4.5	0.0	27.2	2.1	86.6
Bt1 29–44	6.5	37.2	4.0	0.0	30.0	3.0	89.2
Bt2 44–71	6.6	37.0	4.1	0.0	30.1	3.0	89.0
Ck1 71–136	8.1	35.0	0.0	0.0	31.0	3.9	100
			P4. Bhatycalcaric Luvic Phaeozem				
Ap 0–32	6.1	26.6	4.9	0.0	18.4	4.0	81.6
AB 32–60	6.8	30.8	3.8	0.0	23.4	5.0	87.7
Bt1 60–89	6.8	30.9	3.8	0.0	24.3	3.9	87.7

Horizon/ Depth, cm	$pH_{(H2O)}$	CEC	ex. $H_{8.2}$	ex. Al	ex. Ca	ex. Mg	*V*, %
		meq/100 g soil					
Bt2 89–128	6.8	30.6	3.9	0.0	23.1	4.3	87.3
Bt3 128–150	6.7	31.0	3.3	0.0	25.3	3.3	89.4
Ck1 150–180	8.2	37.2	0.0	0.0	34.8	2.4	100
P5. Bhatycalcaric Luvic Phaeozem							
Ap 0–28	6.1	25.1	5.5	0.0	18.0	2.3	78.1
A2 28–43	5.6	27.2	7.6	0.0	16.8	2.5	72.1
ABt 43–66	5.5	31.5	6.8	0.0	20.5	2.8	78.4
Bt1 66–98	5.8	25.5	5.4	0.0	20.3	3.4	81.7
BCk 98–130	7.2	30.6	4.4	0.0	24.9	1.9	85.6
Ck1 130–153	8.2	30.8	0.0	0.0	29.6	1.2	100
P6. Bhatycalcaric Luvic Phaeozem							
Ap 0–28	5.3	26.7	8.3	1.1	16.0	2.2	68.9
A2 28–40	5.4	26.7	8.2	1.2	16.8	1.5	69.3
Bt1 40–63	5.7	30.9	7.1	0.8	21.6	2.1	77.0
Bt2 63–100	5.7	30.5	5.7	0.4	23.0	1.3	81.3
Ck1 100–150	8.1	28.2	0.0	0.0	27.0	1.3	100

Note: CEC is cation exchange capacity; ex. $H_{8.2}$ is total acidity; ex. Al is exchange acidity; ex. Ca is exchangeable Ca; ex. Mg is exchangeable Mg; *V* is base saturation.

Fig. 1. Phaeozem from North Bulgaria – Dark grey forest soil (photo by Koinov et al. 1998).

Fig. 2. Phaeozem from South Bulgaria – Meadow cinnamonic soil (photo by B. Hristov).

High values of soil pH are due to soil profiles, are developing over calcareous sediments with alkaline reactions such as loess and similar soft Quaternary sediments (Hristov 2016).

Figures 1 and 2 show two deep, well-formed soil profiles of Phaeozems from Northern and Southern Bulgaria. The subsurface Bt horizon is commonly referred as clay rich layer significantly altered by pedogenesis, mostly with the formation of iron oxides and clay minerals. Typically clay formation in Phaeozems is *in situ*, but also clay illuviation from surface horizons could be found. This soil layer is usually brownish or reddish due to the iron oxides, which increases the chroma of the subsoil to a degree that it can be distinguished from the other horizons. Therefore, this is an argic horizon, in the middle of the profiles, with high clay content and high CEC.

In deep C horizon there are carbonates with white colour, respectively with high base saturation. The difference between them is reddish colour in the middle because of Mediterranean influence in Southern Bulgaria, and the Phaeozems from the north are deeper.

The cation exchange capacity of soil determines the total capacity of a soil to hold exchangeable cations. This can have a significant effect on its fertility management (Mengel 1993). According to Ganev et al. (1990) classification studied soils are moderately colloidal with average value of CEC about 31.59 meq/100 g soil (Fig. 3 and Table 2). In almost all soil profiles the highest values of CEC are in Bt horizon, because of high clay accumulation from leaching and lessivation in the argic horizon. P1 has the highest content of CEC up to 43.50 meq/100 g soil. The reason for that is parent rock of thick clay Pliocene and Quaternary sediments. All other soil profiles from North Bulgaria spread over clay loess.

Total acidity ($H_{8.2}$) and exchange acidity (Al) are in low quantities. The main reason for that is alkaline reaction and low amount exchangeable cations with acidic functions adsorbed on strongly acid and weakly acid ion exchangers of the soil colloids and lack of adsorbed exchangeable acid ions. The exchangeable acidity (ex. Al) is about zero in most horizons except in P1 and P6. The main presence of total acidity and exchangeable acidity is in surface horizons. This is because rainwater is slightly acidic

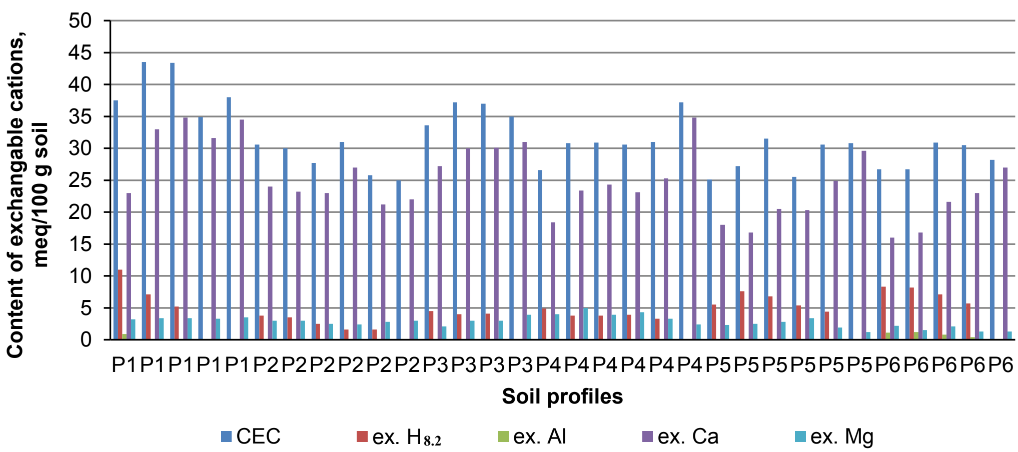

Fig. 3. Soil profiles with graphical values.

Table 2. Descriptive statistic of soil physicochemical properties.

Descriptive statistic	pH	CEC	ex. $H_{8.2}$	ex. Al	ex. Ca	ex. Mg	V%
Mean	6.65	31.59	3.99	0.14	24.98	2.84	87.11
Standard Error	0.16	0.88	0.51	0.06	0.96	0.16	1.68
Median	6.70	30.80	3.95	0.00	23.70	3.00	87.64
Mode	6.80	30.60	0.00	0.00	23.00	3.00	100.00
Standard Deviation	0.89	4.95	2.90	0.34	5.45	0.90	9.51
Range	2.90	18.50	11.00	1.20	18.80	3.80	31.10
Minimum	5.30	25.00	0.00	0.00	16.00	1.20	68.90
Maximum	8.20	43.50	11.00	1.20	34.80	5.00	100.00

Note: CEC is cation exchange capacity; ex. $H_{8.2}$ is total acidity; ex. Al is exchange acidity; ex. Ca is exchangeable Ca; ex. Mg is exchangeable Mg; V is base saturation.

(about 5.7) due to a reaction with CO_2 in the atmosphere that forms carbonic acid.

The number of H and Al ions decreases and the quantity of Ca and Mg ions increases. Cations which are alkaline (non-acid) and therefore raise the soil pH and base saturation in studied soils are mainly Ca and Mg.

High amount of Ca cations in the soil is because it is part of many primary and secondary minerals content. It is usually the dominant basic cation in soil cation exchange reactions, typically accounting for more than 70 % of base saturation (Pagani et al. 2013). Exchangeable Ca reach maximum at 35 meq/100 g, with average content about 24 meq/100 g and averagely 78 % of CEC. It is adsorbed strongly as compared with other exchangeable cations. More clay minerals adsorbed more Ca (Ganev 1989, Sposito 1989, Pavlova et al. 2005b). There is positive correlation between Ca and CEC, pH, and base saturation (0.83, 0.6 and 0.69). The relationship is confirmed for the effective cation exchange capacity, which is due to its stability in different methods of analysis and evaluation (Arsova and Malinova 1995, Malinova 1996, Pavlova et al. 2005a).

Soil pH has good positive statistical correlation with exchangeable Ca (0.6) and base saturation (0.94) (Table 3). There is also negative correlation with total acidity $H_{8.2}$ (–0.93) and exhalable acidity Al (–0.55).

Table 3. Correlation matrix of variables.

Soil indices	$pH_{(H2O)}$	CEC	ex. $H_{8.2}$	ex. Al	ex. Ca	ex. Mg	*V*, %
$pH_{(H2O)}$	1						
CEC	0.12	1					
ex. $H_{8.2}$	**-0.93**	0.00	1				
ex. Al	**-0.55**	-0.13	**0.62**	1			
ex. Ca	**0.60**	**0.83**	**-0.53**	-0.43	1		
ex. Mg	0.05	0.25	-0.05	-0.33	0.14	1	
***V*, %**	**0.94**	0.21	**-0.97**	**-0.66**	**0.69**	0.11	1

Note: In bold, variables are positively correlated (>0.5) or negatively correlated (<–0.5).

The high levels of competing elements, such as Ca, reduce the availability of Mg. Although Ca and Mg share the same exchange processes, Mg sorbs less strongly than Ca to soil colloids and therefore it is more prone to leaching. The average content is about 2.8 meq/100 g with maximum value of 5 meq/100 g. The interesting fact is that Mg does not correlate with all other indices (Table 3).

As it was mentioned above base saturation (%) has high values. It is calculated as the percentage of CEC occupied by base cations Ca, Mg and K. All soil profiles are with Calcaric or Endocalcic qualifiers according WRB classification (IUSS Working Group 2015) with values of base saturation from 70 to 100 %. It is increasing in deepest horizons due to high carbonate content. Consequently, base saturation has positive correlation with soil pH and Ca and negative with total acidity (Table 3).

Conclusion

Phaeozems in Bulgaria are fertile soils with high CEC, high base saturation and favourable soil reaction for crops. These soils are neutral to moderately acidic in surface horizon and slightly leached with pH from 5.3 to 6.7 and alkaline reaction in depth up to 8.2.

CEC varies from 25 to 43 meq/100 g, that is high and similar to most fertile soils such as Chernozems and Kastanozems. The highest values of CEC are in argic – Bt horizon because of high clay content. Studied soils are moderately colloidal with average value of CEC about 31.59 meq/100 g. The content of total acidity and exchange acidity is low. The main reason for that is alkaline reaction of parent rock, because of high content of carbonates. Therefore, exchangeable Ca has high values, up to 35 meq/100 g, which is about 78 % of CEC. All other base cations are in low quantities, Mg varies from 1.2 to 5 meq/100 g. It is determined that variable charges on soil colloids are usually occupied by mainly by Ca and Mg ions. High base cations content means high base saturation. Studied soils have good base saturation from 70 to 100 %.

New statistical analyses were made that show good correlations between soil pH, ex. Ca, and base saturation. There is negative correlation between soil pH, ex. Al and ex. $H_{8.2}$, and also similar negative correlation between base saturation, ex. Al and ex. $H_{8.2}$.

Obtained results show that Phaeozems have good buffer capacity in whole soil profile, with favourable physicochemical properties and high agricultural potential.

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