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Characteristics of soils from the plateau of Kamen briag and the fault-block terrace of the reserve "Yailata"

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Abstract

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Soil characteristics are result of the soil development stages and depend on the intensity and duration of weathering and soil forming processes. Investigations on local environment constituents are associated with studies on the representative soil units and on the morphological, physical, chemical and mineralogical properties of soil varieties. The paper deals with a study of the distribution along profile depth of the free (nonsilicate) forms of elements of Fe and Mn in the most representative soil units along the Northern Black Sea Coast in the region of the plateau of Kamen briag and the fault-block terrace of the reserve "Yailata" with the aim to present the intricacy of soil evolution. The paper presents results of the differences observed in specific patterns of the the content of total Fe_2O_3 and Al_2O_3, as well as in the pyrophosphate extractable free Fe and Mn forms (bound with organic matter) in Leached Chernozem (Karasoluk) and the content of the dithionite extractable free Mn and especially by the content of oxalate extractable Fe in the Fericalcareous soil. As a result, this reflects the soil colour 10YR Hues of the Leached Chernozem (Karasoluk) and 2.5YR Hues of the Fericalcareous soil. There is no correlation of the red soil color and total content of Fe_2O_3 neither in the soil mass nor in the clay. Obviously the red color is determined not from the total content of Fe_2O_3, but from its free forms Fe_o (oxalate), determined by the method of Tamm, and Fe_d (dithionite), determined by the method of Mehra-Jackson. It is established that the content of Fe_d is lower than that of Fe_o. There is a difference from the most soil of Bulgaria, in which $Fe_d > Fe_o$, mainly due to the features of temperature-moisture regimes and presence of carbonates.

Keywords: soils; Fe; Mn; nonsilicate forms; soil process; soil evolution

Introduction

Soil characteristics are results of the soil development stages and depend on the intensity and duration of weathering and soil forming processes, i.e. on the age, chemical composition and resistance to the weathering of soil parent materials, as well as on the influence of climate, plants, relief and human activity. Products of these processes are the free (nonsilicate) forms of elements, released through the destruction of the primary mineral lattices. Their content along depth of the soil profile illustrates the degree of the processes that have occurred during the soil development.

The purpose of this paper is to study the distribution along profile depth of the free forms of Fe and Mn in the most representative soil units along the Northern Black Sea Coast, in the region of the plateau of Kamen briag and the fault-block terrace of the reserve "Yailata" and to present the intricacy of soil evolution. In Dobrudzha plateau, the main soil-forming rocks are the loess, rocky (Sarmatian marls as well as chalks) revelations near the Black Sea Coast, carbonate materials, conglomerates and sandstone. The vegetation in this part of the Balkan-Moesian (Lower-Danubian) forest-steppe province of the Eurasian steppe area is comparatively preserved with relict steppe vegetation includes relatively high numbers of endemic, rare and threatened species, which is the reason for its importance for conservation of biodiversity and the specific habitats and associations belong to the alliance endemic syntaxon for Bulgarian and Romanian Black Sea coasts.

Materials and Methods

Object of the studies were Leached Chernozem Clayic (Karasoluk) (Profile 1), developed on the plateau of Kamen briag, and Fericalcareous soil (Zon and Penkov, 1976) (Profile 2), developed on the fault-block terrace of the reserve "Yailata" (Fig. 1). According to WRB (2015) the first soil is associated as Protovertic Chernozem Clayic and the second one is Calcaric Leptosol (Chromic), respectively. Both soils are developed on the weathered calcareous parent materials *in situ* – mantled loess sediments and limestone under climate conditions contributing prolonged weathering processes. They are formed at different relief and vegetation conditions, consequently, Leached Chernozem Clayic (Karasoluk) is on a flat plain without runoff under steppe grass varieties, and Fericalcareous soil – on the high slop gradient of coastal rock limestone. Leached Chernozem (Karasoluk) is an arable land with grown crops, and Fericalcareous soil is in a virgin area characterized with endemic plants.

Particle size distribution was studied by the method of Kachinskiy (1958). Total content of Fe, Al and Mn was determined by acid dissolving (HF + $HClO_4$) of soil samples (particle size < 0.001 mm); the content of their dithionite, oxalate and pyrophosphate extractable free forms – by the method of Mera-Jackson, Tamm and Bascomb, respectively.

Fig. 1. Matrix of Fericalcareous soil on the fault-block terrace of the reserve "Yailata".

The concentrations of these elements in the obtained solutions were determined by the atomic absorption method. Main soil characteristics are presented on Table 2, and the obtained results of the free forms of Fe and Mn – on Table 3.

Results and Discussion

Despite the intensive development of agriculture in the eastern part of Dobrich region, untouched places by the anthropogenic activities exist. The region is an amaze mosaic of the natural and archeological objects, above it passes one of the main bird's migratory way – Via Pontica. There is coast wet areas of global importance (the most significant winter quarter in Europe for water birds), a relict steppe with more than 400 plants varieties, among them 40 rear and endemic. As a category of the historical place (according act N1047/22.XII.1987) "Yailata" was changed to the protected area (act N822/23.VIII.2002) and was included in the State register of the protected territories with the same name.

Specificity of the atmospheric circulation, radiation and geographical conditions assigns the region as Northern Black Sea climatic region of the Continental-Mediterranean climatic zone. Significant peculiarity of the Black Sea Climate region is comparatively warm and wet winter and hot dry summer. The influence of the sea is prominent 15-20 km inland. Spring is rather cold with frequent influence of cold north-east air translocations. Autumn is warm and dry. Equally distributed during the year with max in November and December, the annual precipitation is 465 mm in Kavarna, 411 mm at horn Kaliakra and 480 mm in Shabla. This delineates the region as the most dried in the country. During summer and autumn there are dried periods continue for 16-30 days enhancing tendency of drought threat.

There is strong wind from north and north-east during the year as follow: during the summer at average wind speed 2.8 m/sec, during the winter 4.6 m/sec (often up to 15-20 m/sec). Percentage of the occurrence of wind below 1 m/sec is at horn Kaliakra 13.5% and at Shabla 29.1% (Table 1).

Duration of sun radiation at Kavarna is 2286 h and at horn Kaliakra 2227 h. Annual radiation is high 5400 MJ/$м^2$ (sum of sun radiation for the period of air above 100°C is 4100 MJ/$м^2$. Mean annual temperature for the region is 11.8°C. An average amplitude of air temperature in Shabla is 9.0°C, at horn Kaliakra – 6.0°C.

The undulating plateau of Kamen briag and the fault-block terrace of the reserve "Yailata" are formed on oolitic, organic, dolomitic and marly limestones. Karst in the region is plain and its development is advanced due to the low slop degree of susceptible calcareous rocks and dense covering with cracks. The old karst is covered with loess sediments

Table 1
Specificity of the main climatic characteristics and radiation in the region

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	
Mean month and annual precipitation, mm													
Horn Kaliakra	38	32	24	30	34	40	25	22	30	42	53	42	411
Shabla	42	36	29	35	40	42	34	30	31	47	60	49	480
Kavarna	40	35	35	40	45	44	29	33	37	38	54	46	465
Mean month and annual wind speed, m/sec													
Horn Kaliakra	8.5	8.3	7.0	5.4	5.2	4.8	5.5	5.8	6.7	7.0	7.6	8.0	6.7
Shabla	4.7	4.2	3.7	3.8	3.6	2.9	2.6	2.9	3.1	3.3	3.7	4.3	3.6
Mean month and annual air temperature, °C													
Horn Kaliakra	0.8	2.0	4.3	9.0	14.6	19.6	22.3	22.5	18.9	14.2	9.4	4.4	11.8
Shabla	0.6	2.2	4.4	9.8	15.7	20.1	22.5	22.1	18.0	13.2	8.9	3.8	11.8
Mean month and annual high air temperature, °C													
Horn Kaliakra	5.2	5.6	8.9	13.2	20.5	24.6	27.5	27.8	23.2	17.8	12.7	7.7	16.2
Mean month and annual low air temperature, °C													
Horn Kaliakra	0.2	0.5	3.6	8.0	14.1	18.6	21.0	21.5	17.5	12.5	7.9	2.7	10.7
Daily mean air temperature, °C													
Horn Kaliakra	2.7	3.1	6.3	10.6	17.3	21.6	24.3	24.6	20.3	15.1	10.3	5.2	13.5
Duration ofsun radiation, hours													
Horn Kaliakra	80	85	124	173	235	293	338	316	241	178	94	70	2227

and its distribution prevails in the region. Denuded karst spreads at coastal areas and forms bare karst fields, locally named „kayratsy". Loess cover in the coastal areas is less than 10 (15) m. Runoff is slight, due to high porosity of loess has mantled the karst limestone and the low slop gradient.

The regional territory of contemporary wave abrasion is 42% of the total affected coastal territory of the country. It is an inherited relict consequence of an ancient slides formation. Formation of the terraced relief is related to the end of Pleistocene, when the level of the ocean decreased due to the glacial period. At the beginning of Holocene Sea level was 90-100 m below the contemporary one. After Wurm during the warm period 10 000 years BP the sea flooded waist coastal valley and transformed it to Holocene terraces.

The studied soils differ in the horizon profile composition: Leached Chernozem (Karasoluk) or Protovertic Chernozem Clayic (WRB, 2015) (Profile 1) is characterized by well developed mollic horizon (0-40 cm) leached of carbonates, transitional Bwk with carbonates accumulation like pseudomicellium and Ck horizon with carbonate concretions. Fericalcareous soil or Calcaric Leptosol (Chromic) (WRB, 2015) (Profile 2) is characterized with no differentiated profile ACk-CRk-R, depth between 10-50 cm and 2.55YR 4/6 and 5YR 6/6 Hues (Fig. 2). The low percentage of humus of calcic mull type, the carbonates content more than 30-45%, the pH (lightly basic) and the saturation of 100% are not correspond to the Terra Rossa soil type. As a result of permanent secondary carbonatization of the profile it is hardly to refer this soil as developed from the relict Terra Rossa. Obviously this is a contemporary developed soil with the high content of amorphous and crystaline Fe forms precipitated as coatings.

The results confirm that the development stages of the profile of Leached Chernozem (Karasoluk) are more advanced, than that of Fericalcareous soil. In the first soil the content of clay and physical clay fractions (particle size < 0.001 and < 0.01 mm, respectively) is higher than in the second one. The Fericalcareous soil is influenced by the process of wind erosion, which results in the lower content of the finer clay and silt fractions (particle size < 0.001 and < 0.01 mm, respectively) and in higher content of the coarser fraction (1-0.25 mm), whereas the content of the fine silt fraction (0.05-0.01 mm) is nearly close. In comparison with Profile 1, the thickness of Profile 2 is smaller and content of $CaCO_3$ is much higher. Probably this fact is associated with the coarser fractions. These features correspond to the differences in the chemical properties. Profile 1 is richer in total content of Fe_2O_3 and Al_2O_3, expressed as a percent of soil mass. The total content of Mn at Ah and Ck horizons of the first soil is close to that at the respective horizons of the second soil, since Mn is associated with the coarser fractions. The total content of Fe_2O_3 and Al_2O_3, expressed as a percent

Table 2
Soil colour, pH, content of $CaCO_3$, some fractions, total Fe, Al and Mn in soil

Horizon and depth, cm	Colour	PH H_2O	$CaCO_3$ %	Clay* %	Physical clay** %	Fe_2O_3%	Al_2O_3 %	Mn mg/kg
Profile 1, Leached Chernozem (Karasoluk), *Protovertic Chernozem Clayic* (WRB, 2015)								
Ap 0 – 21	10YR3/3	7.02	0.00	44.5	71.2	5.27	13.40	935
Ah 21 – 40	10YR3/3	6.82	0.00	44.5	70.9	5.56	14.36	891
AB 40 – 56	10YR4/2	7.30	0.00	43.3	70.9	5.34	14.24	908
Bwk 56 – 71	10YR4/3	7.70	9.04	42.1	69.9	5.06	13.53	814
BCk 71 – 85	10YR5/3	7.79	15.32	39.8	70.1	4.77	1.42	797
Ck 85 – 110	10YR5/6	8.00	22.16	35.4	68.0	4.91	10.95	654
Profile 2, Fericalcareous soil, *Calcaric Leptosol* (Chromic) (WRB, 2015)								
ACk 0 – 40	2.5YR4/6	7.90	45.12	34.3	46.3	4.29	10.45	902
CRk 40 – 60	5YR6/6	8.70	29.84	33.9	46.3	3.97	10.28	622

*Clay – particle size < 0.001
**Physical clay – ∑ of particle size < 0.01 mm.

of the mineral part (i.e. of carbonate free soil), is close in the both soils, the total content of Mn is a little higher in Profile 2. The mineral part of the latter soil is relatively enriched with this element, due to the lost of the finer fractions, containing higher content of Fe and Al.

In fact, there is no correlation of the red soil color and total content of Fe_2O_3 neither in the soil mass nor in the clay. Actually there is no difference in the both soils. Obviously the red color is determined not from total content of Fe_2O_3, but of its free forms Fe_o, determined by the method of Tamm, and Fe_d, determined by the method of Mehra-Jackson.

There are differences in the distribution along depth of the free forms. Their content is expressed as percentage of the total content of the respective element, so the stages of the weathering and soil forming processes are illustrated. In comparison with Fe compounds, Mn ones, released from the primary minerals, are included less actively in the clay minerals. They migrate downward and mainly upward as complexes with humus acids. That is associated with the higher relative part of the free Mn compounds than that of Fe.

Because of the amphoteric character of Fe soils with high pH are rich in free forms of Fe, although the role of $CaCO_3$ to protect the mineral lattices from the destruction (Jokova, 1997). Released from the primary minerals Fe compounds precipitate on the particles of the weathered materials. The sum of the free Fe forms, associated with different soil constituents, is determined by the content of the dithionite extractable iron compounds Fe_d, according to the method of Mehra-Jackson (amorphous, poorly ordered hydroxides or well crystallized oxides). Profile 2 is much richer in the oxalate extractable free forms of iron Fe_o, determined by the method of Tamm (amorphous and poorly ordered hydroxides) (Table 2). A part of the free Fe compounds is of well crystallized forms, probably magnetite, which is not com-

Table 3
Content of free forms of Fe and Mn, expressed as a % of the total content

Horizon and depth, cm	Fe_d %	Fe_o %	Fe_p %	Mn_d %	Mn_o %	Mn_p %	Fe_2O_3/Clay
Profile 1: Leached Chernozem, *Protovertic Chernozem Clayic* (WRB, 2015)							
Ap 0 – 21	No det.	13.85	5.50	43.64	51.34	32.09	0.31
Ah 21 – 40	No det.	11.87	1.44	49.16	63.97	10.77	0.27
AB 40 – 56	No det.	16.85	1.50	46.94	53.55	5.73	0.39
Bwk 56 – 71	16.80	10.67	0.98	59.71	63.39	2.46	0.25
BCk 71 – 85	20.96	10.48	0.84	49.66	48.15	2.26	0.26
Ck 85 –110	18.94	8.76	0.61	49.59	49.50	2.44	0.25
Profile 2: Fericalcareous soil, *Calcaric Leptosol* (Chromic) (WRB, 2015)							
ACk 0 – 40	22.61	55.24	0.70	51.88	31.93	1.55	1.61
CRk 40 – 60	30.48	15.37	0.76	67.58	82.06	2.25	0.45

d, o, p – dithionite, oxalate and pyrophosphate extractable.

pletely dissolved by the dithionite-citrate-bicarbonate reagent and it is extractable by the oxalate one (Vodyanitskii, 2001, 2002). In the upper part of the Leached Chernozem (Karasoluk) or Protovertic Chernozem Clayic (WRB, 2015) and of both horizons of Fericalcareous soil or Calcaric Leptosol (Chromic) (WRB, 2015) the content of Fe_d is lower than that of Fe_o. It is a difference from the most soil of Bulgaria, in which $Fe_d > Fe_o$, mainly due to the features of temperature-moisture regimes and presence of carbonates.

In Fericalcareous soil the content of the dithionite extractable manganese Mn_d is higher, but the content of the oxalate extractable manganese Mn_o is lower at the surface horizon. In this soil the content of the free Mn forms is highest at the bottom, whereas in Leached Chernozem (Karasoluk) – at the middle part, due to their migration to the upper part of the profile. In the distribution of the pyrophosphate extractable forms (bound with humus substances) of iron Fe_p and of manganese Mn_p different trend is observed. The Leached Chernozem (Karasoluk) is richer in these forms, due to the much higher content of organic matter.

Since the Fericalcareous soil (Profile 2) is richer in the free Fe forms than the Leached Chernozem (Karasoluk) (Profile 1), the values of the ratio Fed/clay in the first soil are higher (1.6 and 0.45 at ACk and CRk horizon), whereas in Leached Chernozem (Karasoluk) they are 0.3–0.4 (Table 3). That reflects the soil color. The Hues in ACk and CRk horizons of Fericalcareous soil are 2.5YR and, respectively in Leached Chernozem (Karasoluk) 10YR (according to Muncell SCC, 1990).

Conclusions

The following differences are observed between the characteristics of the well developed Leached Chernozem (Karasoluk) or Protovertic Chernozem Clayic (WRB, 2015) and the affected by erosion Fericalcareous soil or Calcaric Leptosol (Chromic) (WRB, 2015) from the plateau of Kamen briag and the fault-block terrace of the reserve "Yailata", respectively. The first soil is richer in clay and silt fractions, the content of total Fe_2O_3 and Al_2O_3, as well as in the pyrophosphate extractable free Fe and Mn forms (bound with organic matter). The second soil is distinguished by the higher pH and by higher content of $CaCO_3$, as well as by the content of the dithionite extractable free Mn and especially by the content of oxalate extractable Fe. That reflects the soil colour – 10YR Hues of the Leached Chernozem and 2.5YR of the Fericalcareous soil. Probably in these soils the iron mineral magnetite presents.

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