Mineral Composition of Clay Fraction of the Chernozems Spread out in Ovče Pole in Republic of Macedonia

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Summary

The results of mineral composition of the clay fraction of the chernozems spread out in Ovče Pole are presented. The mechanical composition of the soil samples show high domination of the physical clay and clay fractions in the soil separates, what is one of the reasons for strong influence on the physical and physical-mechanical properties of the soil. The clay content is dominant in the soil separates fraction and varies from 23.60% to 56.90%, or 36.23% average. The average content of physical sand and physical clay fractions is 42.20% and 57.80% respectively. Analysis of the mineral composition of clay in its entirety showed that no one of the minerals in the analyzed chernozem samples is not in absolute domination, but there is evident higher presence of clay minerals with 2:1 lattice type (vermiculite, illite and smectites) in comparison with 1:1 lattice type (kaolinite). This shows that our variety of vertical chernozems has little deteriorated physical and physical-mechanical properties compared with typical chernozems.

Key words

chernozems, mineral composition, clay, physical-mechanical properties

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Introduction

Based on the conducted planimetering of the chosen cartographical units of the pedological map (Filipovski, 1982), the areas where chernozems are founded in the R. Macedonia, are amounting to 32,800 ha, or 6.0% of the arable agricultural land (546,000 ha, Statistical Yearbook R. Macedonia), i.e. the chernozems comprise 1.28% of the total area of the R. Macedonia (2,571,300 ha).

The examination of the mineral composition of the clay is very important for the genesis, evolution, classification, and for the physical, chemical and productive properties of the soil. In some of the studies, more authors relate the mineral composition of the clay to some physical and physical-mechanical properties of the chernozems, among them Behar et al.(1988), Boneva et al. (1989),Živković et al. (1967), Filipovski (1980) and Markoski (2008).

Our researches are related to the examination of the mineral composition of the clay in the chernozems in the Ovče Pole region. There is very small number of such researches in our country, and there are only few scientific studies concerned by chernozems mineral composition (Manuševa, 1961; Popovski, 1963; Filipovski, 1973, 1980). Furthermore, with our researches we would like to determine the influence of the parent material (substrate) and the other pedogenetic factors on the evolutionary young soils.

The researches have been conducted along the whole depth of the profiles, including the parent material (substrate C). The obtained data for association of the mineral composition of the clay should be used as classification data for the belonging of the soil type to one or other variety.

Material and methods

The field researches are conducted according to the generally accepted methods in our country (Filipovski et al., 1967). During these researches, data has been collected about the relief, the parent material (substrate), the climate, the vegetation and the other soil forming process. Sixteen soil samples have been taken from four profiles for analysis of the mineral composition of the clay. The soil type is the Chernozems (CH) (WRB, 2006) spread in Ovče Pole valley; the coordinates are 41.52' E and 21.57' N. The following methods were used for analysis of soil materials: mechanical composition was determined with the dispersion of the soil with 1 M solution of $Na_4P_2O_7$x 10 H_2O. First, 10 g of soil sample was put in Erlenmeyer flask, then 25 ml of 1 M $Na_4P_2O_7$x 10 H_2O solution was poured into the flask, left for 12 hours, and then mixed for six hours. Finally the suspension was sieved through a 0.2 mm sieve into the 1000 ml cylinder and then pipetted (Škorić, 1986).

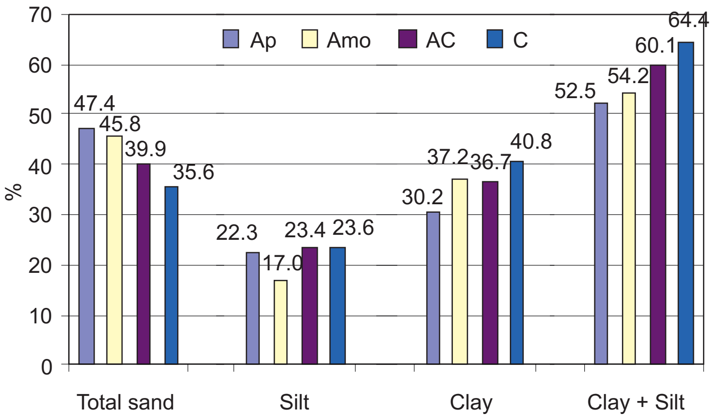
Fractionation of mechanical elements was done by the international classification, using Scheffer & Schachtschabel classifications of soil texture. Classification of soil texture was done by Scheffer & Schachtschabel (Mitrikeski and Mitkova, 2001). Mineralogical composition of clay was determined by diffractometer, brand PHILIPS, type PW 1051 in range $2\theta = 50 \div 60^0$. Mineralogical composition analysis was done at the Mining and Geology Faculty at the University of Belgrade, Republic of Serbia. To determine the clay of each soil sample, two products were made, one of which was untreated, and then filled with glycerine, while the other was annealed at temperatures of 480 ^{0}C for the determined type of clay minerals in the range $2\theta = 30 \div 14^0$ (methods are described by Đurič (1999 and 2002).

Results and discussion

The researched area is located in the central Ovče Pole valley, which represents an open area of the impact of continental and mediterranean climate. The soils develop under the conditions of continental, arid to semiarid climate. This region is one of the driest in the Republic of Macedonia with average annual rainfall of 472 mm with low De Martonne drought index (average 21.0). The index is particularly low (10-15) in June, July, August, and September. Lang's rain factor is also low in the same months (average 37.70). The climate is arid in the three summer months and in September with high potential evaporation (average 731 mm) and high deficit of humidity (average 301 mm). The climate in this region according to Köppen (cited from Ristevski, 1982) is marked as C_2fsax. The dry summers with little rain, the high temperatures, the wind, the cold winters and the existence of $CaCO_3$ are the reason that the aluminosilicates do not fall apart intensively, that there is not intensive foundation of clay, and that no big differences exist concerning the mineral composition between the soil and the substrate. Chernozems studied were A-AC-C; A-ACca-Cca types, and unlike chernozems from other countries (Russia and countries of Panonia Plain) they are shallower, with less marked structure and brighter color. The depth of solum (A + AC) was a solum thickness of 60-80 cm. Horizon A in dry condition is often very dark brown (10 YR 2/2), dark brown (10 YR 3/3) color, and in wet state usually has a black (10 YR 2/1) to very dark gray (10 YR 3/1) color. Transitional horizon (AC horizon) is lighter in color than the A horizon and it contains less humus. Typically, in a dry state AC horizon is gray (10 YR 6/1), light gray (10 YR 7/1) or gray brown (10 YR 5/2), and in the wet state it is usually gray (10 YR 5/1).

Horizon C is lake sediment. It often has weak structure, and a white (10 YR 8/2), light gray (10 YR 7/1), and gray (10 YR 6/1) to gray brown (10 YR 5/2) color. The content of humus is the largest in the surface horizons. The average content for the upper horizon is 2.29%. According to the classification of Škorić (1986) upper soil horizons are poor with humus, and transitional AC and C horizons are very poor with humus. The small content of humus is the result of their intensive processing, low agrology, and burning stubble without applying agro-ameliorative measures. The reaction of soil solution of all tested profiles is below pH 7.0. Horizon A was characterized by a neutral, weakly to moderately alkaline reaction, while a transitional horizon AC and C substrate were characterized with mild to moderately alkaline reaction.

The mineral composition of the clay and the larger particles of the soil depend on the substrate. Chernozems in Ovče Pole valley are developed over the inseparable old quaternary sediments, represented with clay and sand. The largest part of materials of chernozem in this region originates from clay and sand components from neogen sediments, as Mitkova (1998) reported.



Graph 1. Soil separates per horizons of four profiles (average %)

The mechanical composition with an emphasis on clay is of great importance for the physical, physical-mechanical, adsorptive and productive characteristics of chernozem. From the results for soil texture in the horizon C, it can be concluded that physical clay (clay and silt) range from 23.56% to 64.37% and it is predominate in comparison with other fraction of soil separates (Graph 1). Filipovski (1980) reported that high percentage of average clay content in the substrates C is a result of stratification deposits of the chernozems, the differences in the mechanical characteristics, coverage of old geological layers and the influence of the pedogenesis. Also, our results correspond with those of Filipovski (1980) and Mitkova (2003). The results showed that the content of total sand range from 35.64% to 47.40%. In all analyzed soils profiles, fraction silt with range from 16.95% to 23.56% showed the lowest percentage in comparison with other fractions.

Using Scheffer & Schachtschabel classifications of soil texture, it can be concluded that only in 7% of the four tested soil profiles in our investigations, the soil horizon Ap belongs to texture class sandy-clay, while in other 93% to clay. Amo and AC horizons in all soil profiles are classified as clay. In 7% of the tested soil profiles the substrate C belongs to texture class sand clay, 14% to heavy clay and 79% to texture class clay. The results of the soil texture presented in our investigation correspond with those of Kosanović (1954), Penkov (1996), Antonović et al. (1967), Gajić et al. (1997), Filipovski (1996), and Mitkova et al. (2003). The examined soils have relatively favourable mechanical composition. The dominant existence of the fractions physical clay and clay contributes to the small deterioration of the physical and physical-mechanical properties of the chernozem.

Table 1 shows the percentage of the representation of the minerals based on the estimation of the intensity of the main fractions. Theoretically speaking, soil is constituted of all of the minerals. However, the real number and type of the minerals, constituing one soil type is relatively limited.

The data in the Table 1 indicates the following: the chernozems developed from various rocks and differed in their morphology and chemical properties basically, differences in the mineral composition of various profiles and various soil horizons lie in different quantitative relations between the minerals listed above. The quartz fractions dominated by an average of 53.38%, after coming feldspar quartz with an average of 19.10%. The presence of these two fractions (quartz and feldspar) is 72.48%, the remaining 27.52% belongs to other minerals that are present in smaller percentages or are present in traces. The ratio of quartz and feldspar showed what is the difference between the two fractions in different horizons of the examined soils; where is a large percentage of quartz in comparison with feldspar and relations of Q: F is high (25.45).

Scheffer et al. (1956) emphasizes that as in our chernozems and chernozems of Germany in the larger faction has quartz and feldspar.

Concerning the examined chernozems, the mineral composition is inherited from the substrate, and it is not very changed by pedogenesis. The primary and the secondary minerals are

Table 1. Percentage of minerals based on assessment of the intensity of the main fractions (0.05 to 1.0 mm) in chernozems

Profile N°	Depth in cm	Q (%)	F (%)	L (%)	C (%)	GL (%)	X (%)	Q : F
1	0 - 40	64.00	13.30	4.80	0.00	17.70	0.20	4.81
	40 - 60	74.00	12.00	11.00	0.00	2.00	1.00	6.17
	60 - 90	57.50	20.80	11.80	0.00	9.40	0.20	2.76
	90 - 110	35.60	11.50	3.00	34.90	12.90	2.10	3.09
2	0 - 30	76.60	4.40	12.50	0.00	4.30	2.20	17.41
	30 - 60	71.00	17.10	4.10	0.00	7.60	0.20	4.15
	60 - 80	34.40	38.30	2.20	19.60	4.10	1.40	0.90
	80 - 120	19.80	8.70	0.00	66.00	5.00	0.50	2.28
3	0 - 30	65.10	22.00	6.30	0.00	6.40	0.20	2.96
	30 - 50	47.00	45.50	1.80	0.00	4.30	1.40	1.03
	50 - 75	33.00	20.50	3.60	34.00	6.4	2.50	1.61
	75 - 110	26.30	58.90	2.10	8.70	3.20	0.80	0.45
4	0 - 30	45.70	19.50	7.20	12.70	11.00	3.90	2.34
	30 - 60	84.00	3.30	10.70	0.00	1.80	0.20	25.45
	60 - 95	40.70	7.30	1.90	40.70	6.80	2.60	5.57
	95 - 130	61.70	2.60	11.70	13.00	9.90	1.10	23.73

* (Q) - Quartz; (F) - Feldspar; (L) – Minerals of the Liskune group; (C) –Interstratified clay mineral; (GL) – Clay minerals and interstratified mineral; (X) – Other minerals.

settled in the substrate and they are founded by falling apart of the more various rocks which were located over the lake basins. Due to the stated reasons, the mineral composition of the soil is not much different from the one of the substrate and it is almost uniform along the whole depth of the profile. The quartz is most dominant with the average of 52.28%; the feldspars are on the second place with the average of 19.11%. If we make a comparison to the typical chernozems where the percentage of quartz is slightly higher (around 3/4 belongs to the quartz) in comparison to the vertical chernozems, which make a passage to the clay soils, whereby the first minerals are the feldspars, then the other minerals, the quartz etc. The following graphics include a graphical overview of the minerals based on the estimation of the intensity of the main function for the profile number 6.

According to Kostić (2000) the phyllosilicates (clay minerals) are dominant in many soils in the clay fraction (<0.002 mm or 2 microns) and their presence influence the physical, physical-chemical, water-physical and the physical-mechanical properties of the soil (plasticity, stickiness, swelling, contraction, cohesion, induration), the structure of the soil and retention. We have not enough data for the mineral composition of the clay concerning the chernozems in our country. Only Filipovski (1996) has presented data for the two profiles of the chernozems in the Ovče Pole region (village Mustafino).

Table 2 presents the mineral composition of the chernozems obtained by x-ray diffraction analysis.

Results in the Table 2 are given semi quantitatively, thus the presence of certain minerals is indicated by plus (+), which indicate the presence of the individual minerals (+++++) > 70%; (++++) = 50 - 70%; (+++) = 30-50%; (++) = 10-30% and (-) = traces.

None of the minerals in the analyzed chernozems is absolutely dominant, but the greater presence of the clay minerals with lattice type 2:1 (vermiculite, illite and smectite) is obvious when compared to the minerals with lattice type 1:1 (kaolinite). The crystal units of the minerals from the group of smectites are poorly bound, so while moisturizing, water molecules and various ions enter and they move away.

The montmorilonit has active and internal surfaces between the crystal units, so that the ions are adsorbing outside as well as inside (extramicellar and intermicellar adsorption). Because of that, the montmorilonit has high ion adsorption capacity (CEC), high degree of hydration, dispersion, plasticity, stickiness and swelling in moist condition. While drying, the crystal units come closer and the particles decrease, i.e. they contract.

Here we can emphasize that the illite, although it belongs to the same group as the other minerals and the same lattice type, it does not have the same properties. The main characteristic is the distance between the crystal units in its lattice and the firmly bound units with the K-ion. The illite with its properties represents a passage between the smectites and the kaolinite.

The illite has a low capacity of adsorption, very close to the one of the kaolinite 10-40 meq/100 g, and it does not show any signs of swelling, plasticity and stickiness.

The structure of the vermiculite is very close to the one of the illite, but it is different because the K-ions between the crystal units are replaced with other ions. These ions are more weakly bound to the crystal units and they enable greater internal surface. Because of that, the vermiculite has high adsorption capacity and similar to the smectite, it manifests swelling, plasticity and stickiness. Regarding the data in the Table 2, it can be said that profile 2 has almost the same composition of clay mineral (vermiculite, illite and kaolinite) throughout the whole profile, whereby greater presence of the smectites was noticed in the substrate C when compared to the other horizons.

Table 2. Clay mineralogical composition (< 0.002 mm) of chernozems

Profile N°	Horizons, Depth in cm	Smectites	Vermiculite	Illite	Kaolinite
1	Ap 0-40	+	+	++	+
	Amo 40-60	++	+	++	+
	Amo 60-90	++	+	++	+
	AC 90-110	+++	+	++	++
2	Ap 0-30	+	-	-	++
	Amo 30-60	+	-	++	++
	AC 60-80	++	-	+	-
	C 80-120	++	+	+	+
3	Ap 0-30	++	+	++	+
	Amo 30-50	++	+	+	++
	ACca 50-75	++	-	+	++
	Cca 75-110	++	++	++	+
4	Apca 0-30	++	+	++	+
	Amoca 30-60	+++	+	++	+
	ACca 60-95	+++	+	++	-
	Cca 95-130	+++	+	+	-

The profile 2, along the whole depth, comprises all minerals, except for the vermiculite, which is present only in the substrate, while profile 4 is dominated by the smectites in comparison to the other minerals, especially on 30 cm depth. Ciolkosz et al. (2003), exploring five profiles of chernozems from several European countries, concluded that all European chernozems examined in their study had a similar mineral complex of the clay fraction.

Its major components were montmorillonite and illite usually forming mixed structures, whereas kaolinite, quartz, vermiculite and chlorite were present in smaller amounts.

The mineral composition of the clay mostly depends on the stratigraphy of the substrate. In case of layerness and appearance of the lithological discontinuity, it is hard to explain the increase of the smectites in the horizons under 30 i.e. 40 cm (profile 1 and 2). That is mainly a result of other processes (transformation of the other minerals and removal of the minerals).

The values we have obtained from the analysis are very close to the values presented by Filipovski (1996), and similar values for the chernozems in other areas have been presented in the scientific studies of the Antipov-Karataev et al. (1960), Scheffer et al (1956), and Duchaufour (1977), cited by Filipovski (1996).

Lesovaya et al. (2003), examining the pedogenetic, lithologic properties and the mineral composition of the chernozems, spread in the north areas of Russia, determined the polymineral composition of the soil. The clay fraction is mostly dominated by the smectite from 20 to 50 %, following the kaolinite 12 – 26% and the chlorites from 10 to 22%.

The data for the mineral composition speaks for the variety: vertic chernozems with slightly deteriorated physical and physical-mechanical properties in comparison to the typical chernozems. The vertic chernozems, under this or other name, have been mentioned in the classification of soils in more states. Penkov (1979) in Bulgaria describes clay chernozems that make the passage towards the vertisols. In the Romanian classification of the soils from 1976, vertic chernozems have been described. Hraško et al. (1987) in Chechoslovakia describe chernozems reach with clay, which used to be known as a chernozem – vertisols. Duchaufour (1977), according to Filipovski (1996), speaks about vertic chernozems.

Conclusion

Based on the obtained data for the influence of minerals of clay fraction the reasons can be ascertained:

- Mechanical composition of the tested soil is characterized by the domination of the natural clay fractions and clay in separates, which has great influence on the physical and mechanical properties and soils;
- The mineral composition of the examined chernozems is inherited by the substrate, and it is not very changed by the pedogenesis. The primary and the secondary minerals are settled in the substrate and they are formed by falling apart of more different rocks that were located over the lake basins.
- The most dominant is the quartz with the average of 52.28%, whereby the feldspars are on the second place with the average of 19.11%.
- None of the minerals in the analyzed chernozems is absolutely dominant, but it can be seen that there is more clay minerals with the lattice type 2:1 (vermiculite, illite and smectite) when compared to the minerals with lattice type 1:1 (kaolinite). The crystal units of the minerals from the group of the smectites are poorly bound, so that while moisturizing, water molecules and various ions enter between them and they move away.
- The data for the mineral composition speak for variety: vertic chernozems with slightly deteriorated physical and physical-mechanical properties in comparison to the typical chernozems. The vertic chernozems, under this or other name, have been mentioned in the classification of soils in more states.

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