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The origin of montmorillonite in vertisols from the Southern Serbian Pcinja District

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This paper presents research results of the mineral composition of vertisols from Pcinja District in the southern part of the Republic of Serbia. Geological substrates were identified and positioned on the geological map of Serbia, soil profiles (no.1, 4 to 6) were opened and soil samples were taken in order to perform soil analysis. The mineral composition of soil samples was revealed by the X-ray powder diffraction analysis. The results showed that montmorillonite in these vertisols (from Pcinja District) are partially formed by transformation of primary minerals: micas (mica \rightarrow **illite** \rightarrow **montmorillonite),** feldspars (feldspar \rightarrow sericite \rightarrow illite \rightarrow montmorillonite), plagioclases (plagioclase \rightarrow sericite \rightarrow **montmorillonite) and the rest of montmorillonite originate from the parent material.**

Key words: Vertisols, mineral composition, montmorillonite.

INTRODUCTION

Vertisols are automorphic soils with A-AC-C soil profile, class of humus-accumulative soils (Ciric, 1991). Vertisols cover 335 million ha worldwide (WRB, 2006). In Serbia, they cover 780 000 ha mostly in the central region – Sumadija, but they are also found in almost all others parts: eastern (Negotinska Krajina), southern (Vranjska kotlina, Kosovo and Metohija) and northern parts (Vojvodina, around Vrsac and Bela Crkva) (Skoric, 1986). Significant role in forming of vertisols have smectite (montmorillonite) minerals 2:1 type which are formed by resilication or from other minerals *in situ* (Rozanov, 1983). Vertisols are formed on Neogene sediments consisting of carbonate clays and in some parts of Sumadija, Pomoravlje and eastern Serbia, vertisols are formed on calcareous marl parent material (Ciric, 1991).

Two subtypes of vertisols (calcareous and noncalcareous) have been distingished based on soil survey of vertisols from Pcinja District (Golubovic, 2009). The amount of smectite varies in vertisols from different locations. In Sumadija, according to Kostić (2001), mineral composition of clay size fraction is: illite 46.02%, smectite 22.69%, kaolinite 7.66%, vermiculite 5.70% and chlorite 4.07%. According to Filipovski (Cernescu et al., 1970), vertisols from FYR Macedonia аre formed on lake clay and contain up to 70% of montmorillonite minerals, less than 30% of illite and about 10% of kaolinite. Bogunovic (1988) determined that vertisols from the Croatian peninsula Istra contain montmorillonite minerals in concentrations that vary from 60 to 70%, while illite varies from 20 to 25% and kaolinite from 2 to 4%.

Heidari and Mahmoodi (2006) point out that mineralogical study of vertisols in Iran shows dominant part of vermiculite, chlorite and illite, with little smectite as and kaolinite, whereupon these vertisols are referred to

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Table 1. The sampled profiles labels, types and locations.

"non-smectitic vertisols from Iran". There is little data on the origin of montmorillonite minerals in vertisols. The scope of the research presented in this paper was to determine the origin of montmorillonite clay in vertisols sampled in southern Serbian Pcinja District. There is no data on mineral composition of vertisols from this region.

MATERIALS AND METHODS

Four soil profiles were positioned all over the studied region, on locations corresponding to the formation of the vertisols (Table 1). The geological substrates on which vertisol are formed in this area are 400 to 500 m above sea level. Two subtypes of vertisols (based on the Serbian National Classification): calcareous and non-calcareous were identified. Standard methods for studying physical and chemical properties of soil in order to determine the soil type were performed. Mechanical composition of the soil (soil texture) was determined using pipette method; the analysis of carbonate content according to the method of Scheibler; active acidity of the soil, pH in H₂O (1:2.5) and exchangeable acidity, pH in KCl (1:2.5) potentiometrically with a pH meter; hydrolytic acidity according to Kappen method; the sum of adsorbed base cations (S) by calculating; cation exchange capacity (T) according to the method of Bobko – Aksinazi in modification of Alesin (Vorob´eva, 1998) and base saturation percentage (V) by calculation. X - ray powder diffraction and the identification and analysis of clay minerals of two samples from calcareous and two samples of non-calcareous vertisols were performed. The content of the primary minerals in silt-size mechanical fraction of studied soil samples was determined by the X-ray powder diffraction analysis (XRDP), and the processes of the transformation of minerals as well as the origin of the secondary minerals were determined by XRDP of clay-size mechanical fraction.

The X- ray powder diffraction analysis was performed using a PHILIPS PW 1009 diffractometer with Cu-K α radiation (λ = 1.54178 Å). The operating conditions were 35 kV accelerating voltage, 20 mA intensity, with a step size 0.02° and a step interval of 0.5 s, with current of $I = 30$ mA; in the range 2 Θ from 3 to 60°. Clay size mechanical fraction (< 0.002 mm) was separated using decantation method without chemical treatment and then separated with centrifuge. Oriented clay films [air dried (AD), ethylene-glycol saturated (EG) and heated at 550°C] were prepared to identify clay minerals (<0.002 mm). The graphic display of the diffractogram and the analysis were carried out using DRXWin 1.4 software (Martin, 1994).

RESULTS AND DISCUSSION

Basic soil characteristics

The studied soils have high content of clay-size mechanical fraction which varies from 52.32 to 79.76% in calcareous vertisols and from 56.11 to 61.35% in noncalcareous vertisols (Table 2). According to the content of physical clay (<0.01 mm), the studied soils belong to a Wiegner's textural class of medium clay and heavy clay. The hygroscopic moisture (Hy) is in correlation to the content of clay. The chemical analysis of vertisols from Pcinja District shows less acidification in comparison to vertisols from other locations in Serbia which is explained by scarce rainfall in this area. In non-calcareous vertisols, carbonates are removed to a depth below 40 and 50 cm. The calcareous vertisols have high pH which varies from 7.81 to 8.52 (pH in $H₂O$). In non-calcareous vertisols, pH in H_2O is some what lesser in A horizon because carbonates are washed out. Cation exchange capacity of the calcareous vertisols is high which indicates the presence of smectite clays. High values of the sum of adsorbed base cations (S) as well as the base saturation percentage (V) indicate great contribution of base cations to the adsorptive complex of the studied soils (Table 3).

Mineral composition of the soils

Mineral composition of soil profile 1 was obtained using X-ray powder diffraction of the silt-size and the clay-size mechanical fraction (Figures 1 and 2). Parent material of

Label	Depth (cm)	Hy (%)	Diameter of fraction (µm)						
			50-2000	10-50	$5 - 10$	$2 - 5$	2	$<$ 10	Wiegner's textural class
Profile 1	$0 - 20$	6.6	7.7	8.2	5.0	5.5	73.7	84.1	Heavy clay
	20-40	6.9	4.3	8.7	3.2	6.5	77.3	87.1	Heavy clay
	40-65	6.4	3.2	7.6	3.7	7.1	78.5	89.3	Heavy clay
	65-100	5.9	1.8	4.9	3.9	9.6	79.8	93.2	Heavy clay
Profile 4	$0 - 20$	6.7	6.7	11.4	4.5	6.9	70.5	81.9	Heavy clay
	$20 - 40$	6.9	2.9	10.9	3.6	7.3	75.3	86.2	Heavy clay
	40-60	6.3	2.2	5.5	5.2	7.8	79.4	92.4	Heavy clay
	60-80	4.4	22.3	12.7	5.4	7.3	52.3	65.0	Medium clay
Profile 5	$0 - 20$	4.8	23.2	10.3	4.1	6.3	56.1	66.4	Medium clay
	20-40	4.9	18.1	11.4	4.3	7.1	59.2	70.6	Medium clay
	40-60	5.2	15.9	11.4	5.4	5.9	61.4	72.7	Medium clay
	60-80	4.9	17.4	11.8	5.1	6.7	59.0	70.8	Medium clay
Prf.6	$0 - 25$	4.3	15.9	16.5	4.4	5.4	57.8	67.6	Medium clay
	25-50	4.8	15.9	16.1	4.5	5.5	58.0	68.0	Medium clay
	50-80	4.6	14.9	14.7	5.3	5.4	59.7	70.4	Medium clay

Table 2. The mechanical composition of the calcareous vertisols in Pcinja District.

soil profile 1 consists of Pliocene sediments (Neogene period) made of greenish- gray marl, dark grey bentonite clays and grey sandy marl. The most common primary minerals (profile 1) in the silt-size mechanical fraction (Table 4) are: quartz, feldspars and micas; with less calcite and dolomite, and amphiboles in traces. The most common secondary minerals of clay-size mechanical fraction (Profile 1) are: smectite (49 to 62%) and illite (39 to 15%), with less mixed layer minerals (MLM) and chlorites (2 to 4%) and kaolinite (2 to 3%). They are formed from primary minerals of the parent material (Figure 2). Quartz (5.2 to 3%) and feldspars (1 to 4%) (Table 5) are scarce. The results showed that mineral composition of the soil is the same as the mineral composition of parent material which indicates its origin (pliocene sediments). Processes of transformation are obvious in the silt-size mechanical fraction: feldspars [especially albite (Na, Ca plagioclase) transformed to sericite (Figure 1)] and in the clay-size mechanical fraction: illite to montmorillonite. Micas of silt-size mechanical fraction are also transformed, first to hydrоmicas, then to illite, and further there has been an opening of the layers of illite and forming of open illite. The transformation of illite is going in two directions. The first is forming of montmorillonite which leads to the increase of montmorillonite content in clay -size mechanical fraction and the other is forming of MLM (illite/montmorillonite type) (Shrivastava, 2009). Robert et al. (1991) have shown that in some soils in France, illite is related to interstratified clay. This is also described by other authors (Roushani, 2010). Kaolinite originates from feldspars (the kaolinization of feldspars). Clay minerals (smectite, illite) are dominant in soil profile 1 and tend to transform to mixed layer minerals (MLM). According to Ngole et al. (2008) interaction between mineralogy and physical and chemical characteristics of soil is basic to differentiate luvisols, arenosols and vertisols. Vertisols, due to high content of smectite have greater cation exchange capacity, water capacity and bulk density. MLM in soil are of disordered structure with expanding layers of smectite that prevail (Righi et al., 1998).

The increase in content of smectites with depth comes partially of transformation of illite to smectite (which is evident by the presence of MLM of smectite/illite type in the soil) and partially of dispersion of smectite (after removal of carbonates) to deeper parts of soil profile. The second most common clay mineral is illite. The highest concentration of illite is in the surface horizon (0 to 20 cm) and it decreases with depth (from 39 to 15%). High content of illite in the surface horizon is expected for few reasons. It is formed by the transformation of micas (muscovite) which are dominant in clay- size mechanical fraction (24%) of surface horizon of soil profile 1. Decrease of muscovite content with depth is parallel to the decrease of illite content. Content of illite depends on the content of muscovite. Second reason for the

Table 3. Basic chemical properties of vertisols from Pcinja District.

decrease of illite is weathering of illite and forming of open illite which is interstratified with other layers of phyllosilicates and forms MLM of illite/smectite type. Content of MLM is increasing with depth (from 2 to 4%) which also contributes to the decrease of illite. Mineral composition of soil profile 4 was obtained using XRPD of silt-size and clay-size mechanical fraction (Figures 3 and 4). Mineral composition of soil profile 4 indicates correlation with parent material of the profile. Quartz originates from multicoloured sandstone formation which runs from crystalline schists to

Juzna Morava. The rest of it originates from gneiss which forms crystalline schists. Soil profile 4 shows abundance of clay minerals with very little primary minerals. Tendency of transformation to MLM is obvious (Figure 4). Smectites are dominant (44 to 50%), then illite (21 to 31%), calcite and dolomite (12 to 17%), mixed layered minerals and chlorite (3 to 5%), kaolinite (3 to 4%), and the least common are quartz (3 to 4%) and feldspars (1 to 2%).

Orthoclase, albite - oligoclase, epidote, a part of chlorite and muscovite originate from mica schists which together with gneisses make up crystalline schists, and whose transformation has contributed along with other pedogenetic processes, to a high level of smectite and illite (Figure 4). The presence of carbonates is partly induced by the presence of marly sandstones. The rise in content of smectite with depth comes from transformation of feldspars (which is manifested by the presence of MLM) and from transformation of illite [illite \rightarrow MLM \rightarrow smectite (montmorillonite)]. Opposite to smectite concentration of illite decreases with depth (from 31 to21%). High content of illite in surface layer of

Figure 1. X- ray diffractogram of the silt-size mechanical fraction of soil profile 1.

Figure 2. X- ray diffractogram of the clay-size mechanical fraction of soil profile 1.

soil profile 4 comes from high content of muscovite (25% in silt-size mechanical fraction). Content of muscovite decreases with depth which leads to the decrease of illite content (a portion of illite comes from muscovite). Second

reason for the decrease of illite with depth is opening of illite layers and forming of open illite and MLM. This open illite is interstratified with layers of smectite and together they form MLM of illite/smectite type. The content of MLM

Table 4. Mineral composition of silt-size mechanical fraction of vertisols from Pcinja District.

Table 5. Mineral composition of clay-size mechanical fraction in vertisols from Pcinja District.

is the greatest (5%) in the surface layer (0 to 20 cm) and the lowest (3%) in the deepest part of soil profile (60 to 83 cm). Vertisols of soil profile 4 are characterised by high content of smectite and low content of feldspars and quartz in clay-size mechanical fraction.

Carbonates of soil profile 4 are of primary and secondary origin, and they are partially formed by the deposition of Ca out of plagioclase (albite contains about 10% of Ca), and partially from the parent rock (marl sandstone) (Figures 3 and 4).

Figure 3. X-ray diffractogram of the silt-size mechanical fraction of soil profile 4.

Figure 4. X-ray diffractogram of clay-size mechanical fraction of soil profile 4.

The genesis of minerals of non-calcareous vertisols

The rim of Vranje basin is formed of crystalline schists consisting of gneiss and mica schist with lenses of chlorite schists. Among these rocks and Juzna Morava, there are formations of multicoloured sandstones, marl sandstones and tuffs that alternate. All these rocks have important influence on mineral composition of soil profile

Figure 5. X-ray diffractogram of the silt-size mechanical fraction of soil profile 5.

Figure 6. X-ray diffractogram of clay-size mechanical fraction of soil profile 5.

5 (parent material has complex geological structure). XRPD of soil profiles 5 shows primary minerals: quartz, orthoclase, plagioclase (albite), muscovite, chlorite, calcite and dolomite (Figure 5). These primary minerals originate from rocks that make the rim of Vranje basin (gneiss and mica schist with lenses of chlorite schists). Calcite and dolomite originate partly from marl sandstones and partly are formed as secondary minerals due to the pedogenetic processes. Feldspars (especially plagioclase that is albite (Na-Ca plagioclase) are transformed to sericite in the silt-size mechanical fraction; illite is transformed into montmorillonite in the clay-size

mechanical fraction. These processes are reflected through the increase of montmorillonite in clay-size mechanical fraction and in forming of mixed layer minerals (MLM). In silt-size mechanical fraction, muscovite is transformed to hydromica (illite) and further to open illite. Transformation goes in two directions; first, towards forming of montmorillonite (and increase of content of montmorillonite in clay-size mechanical fraction), and second, toward forming of MLM illite/montmorillonite type (and increase of MLM content) (Figure 6).

Kaolinite is of secondary origin – formed by

Figure 7. X-ray diffractogram of the silt-size mechanical fraction of soil profile 6.

kaolinization of alkaline feldspars and plagioklase.

Secondary minerals

Smectite (44 to 54%), illite (26 to 38%), MLM and chlorite (3.9 to 6%), kaolinite (4 to 7%), (Figure 6) come from primary minerals which are closely related to parent material of the soil profile. Quartz and feldspars are the least present (Table 5). Clay minerals (smectite and illite) are the most abundant in soil profile 5 and tend to transform to MLM. MLM are of disordered structure with dominant expanding layers of smectite. Rise in content of smectite with depth is partly caused by transformation of muscovite to illite and further to smectite (which is evident by the presence of MLM of illite/smectite type), and partly, by high dispersity and hydrophilic nature of smectite which is transferred from the surface horizon to the lower parts of soil profile which leads to differentiation of mineral composition of soil profile especially considering content of illite and smectite (Roushani, 2010). The second most common is illite with highest content in the surface layer (0 to 20 cm), and with depth it decreases from 26 to 38%. A high content of illite is predictable in the surface layer due to few reasons. Micas (muscovite) are the most abundant in the surface layer of soil profile 5 (27% of silt-size mechanical fraction) and they transform into illite. Decrease in the content of mica (in silt-size mechanical fraction) with depth causes decrease in the content of illite. Second reason for the decrease of content of illite is "opening of illite layers" and forming of open illite, and with the loss of K it is transformed or interstratified (Roushani, 2010).

Parent material of soil profile 6 is made of primary minerals

Quartz, feldspars, micas, amphiboles, and also of calcite and dolomite (of Pliocene sediments). XRD analysis of clay-size mechanical fraction revealed the following mineral composition: smectite (47 to 52%), illite (30 to 41%), calcite (3 to 8%), MSM and chlorite (3 to 8%), kaolinite (2 to 3%), quartz (1 to 3%) and feldspars (1.5 to 3%) (Figures 7 and 8). They are characteristic of Pliocene sediments. The content of chlorite and MLM shows influence of crystalline schist from the rim of the basin of which chlorites originate. Clay minerals (smectite and illite) are dominant in soil profile 6 while primary minerals are scarce. Transformation of micas to MLM (mostly of disordered structure with dominant expanding layers of smectite) is well expressed. Increase in smectite content with depth comes partly from transformation of feldspars (which is evident from MLM), and partly from transformation of illite to MLM (illite/vermiculite) and further to smectite (montmorillonite). The increase in content of smectite in the deeper parts of soil profile comes partly of its dispersity. Quartz and feldspars (orthoclase) are in connection to the layers of yellow sand which originates from the crystalline schist from the rim of the Vranje basin. Feldspars tend to transform to sericite and to hydromicas (illite) which contributes to the increase of montmorillonite content of soil profile 6. Micas of the silt-size mechanical fraction (Figure 7) are also transforming to hydromicas (illite) and further to smectite (montmorillonite) parallel with forming of "open illite" and interstratified layers of MLM.

Transformation of illite to smectite influences the

Figure 8. X-ray diffractogram of clay-size mechanical fraction of soil profile 6.

increase in smectite content (Figure 8). Dispersity of smectite directs it from the surface to the deeper layers of soil profile and it causes the highest level of smectite in the deepest parts of soil profile. Opposite to smectite, the second most abundant secondary mineral - illite is decreasing with depth. The highest concentration of illite is in the surface horizon (41%) and the lowest in the deepest parts of soil profile (30%). High concentration of illite in the surface layer comes from the high concentration of muscovite in the same layer (23% of the silt-size mechanical fraction). Decrease in muscovite content with depth induces the decrease in illite because a part of illite is of muscovite origin. The second reason for the decrease of illite with depth is opening of illite layers and forming of "open illite" and MLM. These "open illite" is interstratified with smectite layers and formed MSM of illite/smectite type. Content of MLM is the highest (8%) in the middle of soil profile (25 to 50 cm) and the lowest (3%) in the surface layer. Despite the low content, they tell a lot about transformation of primary minerals. Characteristics of vertisols depend upon the characteristics of parent material. Due to limited hydrolysis, silica contributes to the stability of smectite and illite which originate from parent material (Nordt et al., 2010).

Conclusions

The results of the analysis of the mineral composition of the vertisols from Pcinja District have shown that montmorillonite originates partly from transformation of different primary minerals and partly it is inherited from the geological substrate. The most common transformations are transformations of mica and plagioclase through illite and sericite to montmorillonite. The geological profile of the region is very heterogeneous. It can also be observed from different types of transformations of minerals from studied soil profiles which cause different origin of montmorillonite clay in vertisols from Pcinja District. Part of montmorillonite (soil profile 1) originates from andezite micas and crystalline schists (mica \rightarrow illite \rightarrow montmorillonite), fragments of greywacke (plagioclase \rightarrow sericite \rightarrow montmorillonite) and from tuffogenic material. Another part is inherited from the redeposited sediments in freshwater environment during Miocene. In vertisols that are represented by the soil profile 4, montmorillonite is partly connected with the transformation of the grus layer (conglomerates and feldspathic greywacke) where micas and plagioclase transform to montmorillonite. The other part of montmorillonite originates from the layer of subwater slides consisting of packets of muddy sediments with inclusions of packets of yellow sandstones. Montmorillonite of the vertisols represented by the soil profile 5 originates partly from the transported material typical for all river courses with a steep longitudinal profile.

The origin of the montmorillonite depends on the geological composition of the river basin, and in this case those are biotite-muscovite gneiss and mica schists. Therefore, montmorillonite is formed by transformation of

micas, plagioclase and vermiculite. The origin of the montmorillonite of the soil profile 6 is connected to the primary minerals of the Pliocene sediments. Forming and high content of montmorillonite is predictable, for montmorillonite comes mostly from direct transformation of illite (micas \rightarrow illite \rightarrow montmorillonite and feldspars \rightarrow sericite \rightarrow illite \rightarrow montmorillonite). Smaller portion of montmorillonite is formed out of vermiculite (biotite \rightarrow vermiculite \rightarrow montmorillonite).

REFERENCES

- Bogunović M (1988). Vertisols of Croatia. Doctoral Dissertation, Zagreb Ciric M (1991). Pedology. Svjetlost - Zavod za udzbenike i nastavna sredstva, Sarajevo. p. 307.
- Vorob´eva L (1998). Chemical analysis of soil. Moscow University Press, Moscow.
- Golubovic S (2009). Characteristics of Vertisols from Pcinja District. Doctoral Dissertation, Belgrade.
- Filipovski G (1970). Smonitzas of Yougoslavia. In memoriam N.C. Cernescu and M. Popovat , Geologikal Institute, Pedology, Bucharest, no 18.
- Heidari A, Mahmoodi S (2006). Mineralogical characteristics and some physical indices of non-smectitic Vertisols from Iran. Geopysical Research Abstracts, Vol 8, EGU06-A-02012.
- IUSS Working group WRB (2006). World reference base for soil resourses 2006. World Soil Resources Reports No. 103. FAO, Rome
- Kostic N (2001). Mineralogical study of some important soil types of Vojvodina and central Serbia. X Kongres jugoslovenskog drustva za proucavanje zemljista, Vrnjacka banja.
- Martin VP (1994). DRXWin 1.4 a computer program: A graphical and analytical tool for powder XDR patterns, University of Valence, Faculty of Chemistry, Valenca.
- Ngole VM, Ekosse GE (2008). Physico-chemistry and mineralogy related to productivity of arenosol, luvisol and vertisol. Iranian J. Sci. Technolo. Trans. A, 32(A2): 99-108.
- Nordt LC, Driese SD (2010). New weathering index improves paleorainfall estimates from Vertisols. Geol., 38(5): 407-410
- Righi D, Terribile F, Petit S (1998). Pedogenic formation of high-charge beidellite in a Vertisol of Sardinia (Italy). Clays Clay Miner., 46(2): 167-177.
- Robert M, Hardy M, Ellas F (1991). Chrystallochemistry, properties and organization of soil clays derived from major sedimentary rocks in France. Clays Clay Miner., 26: 409-420.
- Roushani G (2010). Effect of exhaustive cropping on potassium depletion and clay mineral Transformations. 19th World Congress of Soil Science, Soil Solutions for a Changing World, 1 – 6 August 2010, Brisbane, Australia.
- Rozanov BG (1983). Soil morphology. Moscow University Press, Moscow, pp. 320.
- Shrivastava VS (2009). X- ray Diffraction and Mineralogical Study of Soil: A Review, J. Appl. Chem. Res., 9: 41-51
- Skoric A (1986). Genesis, evolution and classification of soil. Zagreb