

Ćirić, V., Prekop, N., Šeremešić, S., Vojnov, B., Pejić, B., Radovanović, D., Marinković, D. (2023): The implication of cation exchange capacity (CEC) assessment for soil quality management and improvement. *Agriculture and Forestry*, 69 (4): 113-133. doi:10.17707/AgricultForest.69.4.08

DOI: 10.17707/AgricultForest.69.4.08

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## **THE IMPLICATION OF CATION EXCHANGE CAPACITY (CEC) ASSESSMENT FOR SOIL QUALITY MANAGEMENT AND IMPROVEMENT**

### **SUMMARY**

Soil consists of mineral and organic matter, possessing both chemical and physical, mineralogical and biological properties that provide a medium for plant growth and is therefore one of the most important conditions for agricultural production. On the other hand, soil cation exchange capacity (CEC) is a measure of the total capacity of soil to retain exchangeable cations and indicates the negative charge per unit mass of soil. Cation exchange capacity (CEC) is one of the many properties possessed by the soil, but its importance for the soil is multiple, which is particularly reflected in its ability to maintain soil fertility through binding and preventing the loss of cations from the soil due to binding to soil colloids. Cation exchange is a reversible reaction. CEC prevents the loss of nutrients and soil leaching, affects the availability of nutrients for plants, and serves as a basis for determining the required amounts of fertilizers. CEC in soil depends on the content of clay minerals and organic matter. Organic matter is the main source of CEC in sandy soils. Because of the different methods for estimating CEC, it is important to know the intended use of the data. For soil classification purposes, soil CEC is often measured at a standard pH value (pH 7). Since the value of CEC is a dependent variable property of the soil, its value depends on the content of clay minerals, organic matter, fertilization and pH value. Any change in soil properties leads to changes in CEC values, and therefore to changes in soil fertility.

**Keywords:** cation exchange capacity, CEC, agriculture, soil, organic matter, clay

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Notes: The authors declare that they have no conflicts of interest. Authorship Form signed online.

Received: 12/09/2023

Accepted: 17/11/2023

## INTRODUCTION

Soil Cation Exchange Capacity is a very complex indicator that reflects a subset of soil physical and chemical properties of different individual values, and its interpretation can significantly improve agricultural production. This analysis is not included in the standard set of soil tests, but the values obtained can indicate the properties of the soil and the processes that are taking place. Of particular interest is the CEC monitoring of intensive vegetable production and seedling production. A correct interpretation of the CEC is therefore essential in order to take the appropriate measures to ensure successful production. Soils also have a distinct impact on human health (Brevik and Sauer, 2007), therefore soil contaminants constitute a known global problem and more knowledge is needed regarding their behavior as well as their pathways to humans (Abrahams, 2002; Semedo, 2017; Babec *et al.* 2020). The intensive use of land during the last decades has greatly influenced the change in its physical, chemical and biological properties (Šeremešić *et al.* 2017; Vojnov *et al.* 2019; Vojnov *et al.* 2020a; Kraamwinkel *et al.* 2021). In recent years, numerous authors have warned about the serious consequences of soil degradation that can result from its irrational use (Obalum *et al.* 2017; Semedo, 2017; Šeremešić *et al.* 2021a; Ferreira *et al.* 2022). Cation exchange capacity (CEC) is a soil property that allows it to bind positively charged ions (cations). In another words is a measure that expresses the ability of the soil to adsorb cations, and corresponding with plants capability of absorbing nutrients through the roots in ionic form (Jones and Kathrin, 2016). This is a very important property of the soil that affects the stability of structural aggregates, availability of nutrients for plants, regulates pH of the soil, as well as the reaction of the soil affected by fertilization and the addition of other ameliorants (Hazelton *et al.*, 2007). Clay minerals and components of soil organic matter contain a negative charge on their surface, which is why they adsorb and retain positively charged ions (cations) by electrostatic forces. This type of charge is of great importance for supplying plants with nutrients because many nutrients in the soil are found in the form of cations, such as magnesium ( $Mg^{2+}$ ), potassium ( $K^+$ ) and calcium ( $Ca^{2+}$ ) and other elements. In general, soils that contain a higher degree of negative charge are more fertile soils because they have the ability to bind and retain larger amounts of cations (McKenzie *et al.*, 2004). However, even on soils with a low capacity for cation exchange (CEC), high-yielding crops can be grown, if adequate and timely agrotechnical measures are applied. The major ions associated with soil CECs are the exchangeable cations of calcium ( $Ca^{2+}$ ), magnesium ( $Mg^{2+}$ ), sodium ( $Na^+$ ), and potassium ( $K^+$ ) (Rayment *et al.*, 1992) usually referred to base cations. In most cases, summing the analyzed base cations provides an adequate measure of CEC. However, as soils become more acidic, these cations are replaced by  $H^+$ ,  $Al^{3+}$  and  $Mn^{2+}$  cations and common analytical methods will produce CEC values much higher than what is expected (McKenzie *et al.*, 2004). This cation exchange should be included when evaluating base cations and this measurement is then called effective cation exchange capacity (ECEC). Cation exchange capacity (CEC) of soil primarily

results from clay and organic matter content. Soils contain, to a greater or lesser extent, silicate clay minerals that contain silicon in their composition. Each particle of clay consists of individual layers or sheets, since clay minerals in addition to silicon dioxide contain  $Al^{3+}$  ions, the total charge of clay minerals is negative (Miljković, 2005). The exchange of a silicon ion with aluminum in the crystal lattice is called an isomorphic exchange. Soil as a natural medium does not contain a negative charge due to the fact that the negative charge of clay minerals and colloidal particles of organic matter is in balance with the positive charge of cations (Brown *et al.*, 2007), the negative charge of clay colloids associated with the isomorphic exchange of cations in the crystal lattice is considered is unchanged, regardless of changes in pH value.

### **IMPORTANCE OF CATION EXCHANGE CAPACITY (CEC) IN SOIL**

Cation exchange capacity (CEC) is one of the many properties possessed by the soil, but its importance for the soil is multiple, which is particularly reflected in its ability to maintain soil fertility through binding and preventing the loss of cations from the soil due to binding to soil colloids. Cation exchange is a reversible soil characteristic (Nešić *et al.*, 2015). Preventing the loss of nutrients and soil leaching affects the availability of nutrients for plants and serves as a basis for determining the required amount of fertilizers. The interpretation of this property is based on the assumption that the greatest influence on CEC values in soil exerted the content of clay and organic matter (Hadžić *et al.*, 1995). Organic matter is the main source of CEC in sandy soils (Johnson, 2002). In the soils of Vojvodina, the most common clay minerals belong to the illite group, and the cation exchange capacity is most accurately represented by the fact that 1 g of montmorillonite has an active surface of  $700\text{ m}^2$  with a negative charge, which is why it is able to bind huge amounts of nutrient cations and positively charged radicals from organic compounds, where are first retained, and then subjected to microbiological degradation (Nešić *et al.*, 2015). The average content of humus in the soils of Vojvodina is 3% (Manojlović 2008). For this reason, it is important to study and define the physical and chemical properties of soil, as well as the content of organic matter and clay, as the most important factors of cation exchange, not only to preserve the current state, but also to improve and improve the state of soil fertility. Therefore, it is of crucial importance to study and understand the interrelationships of clay, humus content and their influence on CEC, because soil fertility and its ability to resist degrading changes depends on these properties. CEC is conventionally expressed in  $\text{mec}/100\text{ g}$  (Rengasamy and Churchman, 1999), which is numerically equal to centimoles of charge per kilogram of exchanger ( $\text{cmol}(+)/\text{kg}$ ). The capacity of cation exchange in different types of soil varies in a wide interval from 1-2  $\text{cmol}/\text{kg}$  to more than 100  $\text{cmol}/\text{kg}$  of soil, most often CEC in soils is in the range of 25-35  $\text{cmol}/\text{kg}$  of soil, while in the arable layer of loamy and clayey soils in Serbia that have a low humus content varies in the range of 20 to 40  $\text{cmol}/\text{kg}$  of soil (Dugalić and Gajić 2012).

The content of  $\text{CaCO}_3$  in the soil is very important, and it is especially important for CEC, because calcium in the soil affects the physical and chemical properties, in the form of Ca-humate, as a neutralizer or buffer. Soils that contain a large amount of kaolinite-type clay have a CEC in the range of 1-10 Meq/100 g, while soils that contain illite-type clay and smectite in the range of 25-100 Meq/100 g, organic matter has the capacity to exchange cations in which amounts to 250-400 Meq/100 g (Moore 1998). A high soil cation exchange capacity indicates that the soil has a high content of clay and organic matter, which further causes better water and nutrient retention than soils with a low CEC. Table 1. Shows the value of the cation exchange capacity defined according to (Hazelton *et al.*, 2007).

Table 1. Cation exchange capacity value (Hazelton *et al.*, 2007)

Value	CEC cmol <sub>(+)</sub> kg <sup>-1</sup>
very low	<6
Low	6–12
Medium	12–25
High	25–40
very high	>40

### THE EFFECT OF PH VALUE ON THE CATION EXCHANGE CAPACITY (CEC) IN THE SOIL

Because of the different methods for estimating CEC, it is important to know to use and interpret the obtained results. Therefore pH value of the soil, which further affects the availability of nutrients for the plant is considered of the most important soil properties that affects CEC. Cation exchange capacity can be expressed through different methods (Chapman, 1965; Sumner and Miller, 1996), however each of the methods expresses the assessed material and chemical conditions, especially the pH of the medium. Most methods involve saturating negative exchange sites with cations that form outer sphere complexes such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ , then removing excess cations using an unbuffered solution and determining the amounts retained in the soil (Choo *et al.*, 2016). An indirect method to calculate cation exchange capacity (CEC) is to sum exchangeable bases ( $\text{SB}=\text{Ca}^{2+}+\text{Mg}^{2+}+\text{K}^++\text{Na}^++\text{NH}_4^+$ ) + exchangeable  $\text{Al}^{3+}$  and potential acidity ( $\text{H}^++\text{Al}^{3+}$ ) extracted with appropriate solutions (Donagemma *et al.*, 2011). For soil classification purposes, soil CEC is often measured at a standard pH value (pH 7). Examples are the ammonium acetate method of Schollenberger (1927) buffered at pH 7 and the barium chloride-triethanolamine method of Mehlich (1938) buffered at pH 8.2. Such CEC measurements can result in values that are very different from soil CEC values measured at the pH present in the field (effective CEC or CECE), especially in acidic soils with pH-dependent CEC. If a pH-buffered CEC measurement is required (e.g., for regulatory or soil classification purposes), ammonium acetate buffered to pH 7 is the recommended procedure, CEC determined by this method tends to be less than 3 cmolc/kg for sandy soils with low organic matter content up to more than

25 cmolc/kg for soils with a high content of certain types of clay minerals or organic matter. For an accurate measure of soil CEC in field conditions (Gillman, 1979, Gillman and Sumpter, 1986; Rhoades, 1982) proposed using a method using  $\text{BaCl}_2$ . This method provides an estimate of the soil's capacity to retain base cations (CECb) under field conditions. To estimate the effective CEC (CECE), exchangeable Al is obtained by extraction with 1 M KCl (Bertsch and Bloom, 1996). Soil testing laboratories do not provide direct data for CEC, but data are obtained by recalculating CECsum, based on the amounts of extracted  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$  obtained by laboratory methods (Ross *et al.* 2009). In soils that are rich in  $\text{Na}^+$ , the resulting extracted sodium is added to the calculations. If the soil pH is less than pH 6, the value of substitutional acidity is added to the sum of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$ , which further leads to the conclusion that significant amounts of exchangeable  $\text{Al}^{3+}$  ion may be present.

### MUTUAL INFLUENCE OF CATION EXCHANGE CAPACITY AND FERTILIZERS

It is known that soil reaction depends on the amount and nature of the clay fraction, as well as on the presence and concentration of common cations and anions in the soil solution (Tessier *et al.*, 1999). The fine fraction of clay essentially ensures the regulation of the physico-chemical properties of the soil, and also has a significant role in water retention as well as the bioavailability of nutrients (Daoud *et al.*, 1992). The surface properties of soil components that have a significant role in the adsorption and retention of cations in the soil can be expressed through cation exchange capacity (CEC) or through the specific surface area of clay fractions (SS). The specific surface area of the clay fractions is determined using an organic molecule such as ethylene glycol monoethyl ether (EGME) which strongly adsorbs on the surface of the clay particles (Ciesielski *et al.*, 1997). CEC is measured by measuring the electrical conductivity of the surface components of the soil (Charlet, 1999). Knowledge of the capacity for cation exchange, the specific surface area of clay fractions, as well as the content of organic matter and the pH value of the soil are of great importance for the proper management and use of the soil, but also for the correct determination of the amount and use of fertilizers. Therefore, the addition of organic material is likely to increase the CEC of the soil over a period of time. On the other hand, soil CEC can also decrease over time, either naturally or by acidification caused by the addition of physiologically acidic fertilizers or decomposition of organic matter (McKenzie *et al.* 2004). Nitrogen mineral fertilizers used in agricultural production are key to achieving high yields, while knowledge of cation exchange capacity is necessary for quality soil management, it is especially important to point out that it is necessary to determine the content of organic nitrogen in the soil, which could be mineralized during vegetation period and, based on that, give a recommendation for fertilization with mineral nitrogen fertilizers, all with the aim of avoiding environmental pollution given that mineral forms of nitrogen in the soil, such as the  $\text{NH}_4^+$  ion, can bind to the absorptive complex, while mineral

forms of nitrogen in the form of  $\text{NO}^{3-}$  and  $\text{NO}^{2-}$  cannot bind, and if they are not absorbed by plants and microorganisms, they are washed into the groundwater (Kastori, 2005). Research results (Czarnecki *et al.*, 2014) show that the long-term use of N, P, K fertilizers has significant effects on soil properties, during the study it was found that fertilization with N, P, K fertilizers has a significant effect on the reduction of soil pH. The decrease in the pH value of the surface layer of the soil when using mineral fertilizers can be attributed to the processes of nitrification and acidification stimulated by the continuous application of mineral fertilizers, as well as the release of  $\text{H}^+$  ions from the root system of plants (Liang *et al.*, 2012). In the treatments where N fertilizer was applied, a slight difference in the pH value was observed compared to the initial value, while it was determined that the application of N, P, NP and NPK fertilizers significantly affects the pH value compared to the control in April when the analysis was done, however a significant difference in the reduction of pH value was observed when observing the control and treatments with N and P fertilizers in the month of August, while significant differences in the change in pH when applying only N fertilizer or only P fertilizer did not indicate significant differences in the change in pH value for November (Czarnecki *et al.*, 2014). The continuous application of ammonia fertilizers leads to a lowering of soil pH (Schwab *et al.*, 1990), which was proven by a study (Tsadilas *et al.*, 2005), that indicated that the use of ammonia fertilizers has a greater effect on soil acidification than the application of nitrate fertilizers. Research conducted by Liu *et al.* (2007) proved that the application of ammonia fertilizers in leads to a lowering of the pH value of the soil from 4.51 to 4.07. The main mechanism of soil acidification with the use of ammonia fertilizers is the release of  $\text{H}^+$  ions in the nitrification process, as well as the subsequent leaching of  $\text{NO}^{3-}$  (Barak *et al.*, 1997). The addition of fertilizers to the soil increases the concentration of the soil solution, which further results in increased plant nutrition, which is reflected in an increase in plant mass and yield, and also in an increase in the mass of crop residues returned to the soil (Haynes *et al.*, 1998). Research obtained by Raun *et al.* (1998) as well as (Halvorson *et al.*, 1999) showed an increase in the level of organic C in the soil with the application of N fertilizers. According to research Jagdish *et al.* (2011), the impact of long-term application of synthetic N fertilizers on soil organic matter has been questioned. The hypothesis that long-term application of N fertilizers leads to a decrease in soil organic carbon. Data from 135 studies of 114 long-term experiments located at 100 sites worldwide, over decades, under a range of land management and climate regimes, were used to quantify changes in soil organic carbon (SOC) and soil organic nitrogen (SON) Jagdish *et al.* (2011). Published data from a total of 917 and 580 observations for SOC and SON, representatively, from control (unfertilized or zero N) and N-fertilized treatments (synthetic, organic, and combined), were analyzed using SAS mixed model and meta-analysis. The results show a decrease of 7 to 16% in SOC and 7 to 11% in SON without fertilization with N fertilizers. In soils that received synthetic fertilizer N, the rate of SOM loss was reduced. Fertilizer time response ratio, which is based

on changes in pairwise comparisons, showed an average increase of 8 and 12% for SOC and SON, respectively, after application of synthetic fertilizer N. Addition of organic matter (i.e., manure) increased SOM content, on average, by 37%. This paper shows a general decline in SOM for all long-term sites, with and without the application of synthetic N fertilizers. However, the analysis also shows that in addition to their role in improving crop productivity, synthetic N fertilizers significantly reduce the rate at which SOM is reduced in agricultural soils, worldwide. Research (Messiga *et al.*, 2013) also proved the increase in organic C content when increasing concentrations of N fertilizers were added to the soil. An increase in soil organic carbon content in the layer (0–15 cm) by 7.7% was observed in treatments where mineral fertilizers were added to the soil in contrast to the control (Liu *et al.*, 2005). Similar results were obtained in long-term studies where it was proven that low doses of N fertilizers had a weak effect on the increase of organic C in the soil compared to the control (1.14 vs. 0.03 mg ha<sup>-1</sup> year<sup>-1</sup>), while medium and high doses significantly influenced the increase in organic C (Corg) content, which ranged from 0.45 to 0.49 mg ha<sup>-1</sup> year<sup>-1</sup> (Mazzoncini *et al.*, 2011). The long-term application of manure and mineral fertilizers, either alone or in combination with these fertilizers, has seen a significant increase in the content of organic matter in the soil, which leads to the conclusion that the application of mineral fertilizers has a stimulating effect on microbiological activity, whereby the organic matter of the soil decomposes, which leads to an increase in the availability of nutrients matter for plants, increase in above-ground mass and yield, and therefore to a greater amount of crop residues that are returned to the soil (Gong *et al.*, 2009). According to (Cakmak *et al.* (2010), the application of phosphorus fertilizers in a period of 40 years caused a decrease in soil pH and an increase in CEC. Research conducted by Schjonning *et al.* (1994) showed an increase in CEC values by 11% when using fertilizers compared to control plots. The application of nitrogen in the form of KAN fertilizer or in combination with the NPK complex raises the level of CEC in the soil, which can be explained by the colloidal retention of applied Ca<sup>2+</sup>, NH<sup>4+</sup> and K<sup>+</sup> ions (Radulov *et al.*, 2011), and the content of organic C, which affects CEC soil, where a positive linear relationship between these two soil components was observed (Rashidi *et al.*, 2008). Unlike other studies, research (Bationo *et al.*, 2007) found a negative linear relationship between pH value and organic C content, with two possible explanations for these negative observations: the first is that the accumulation of organic matter does not necessarily affect to a decrease in pH value, and another explanation is that other mechanisms affecting the change in pH are more dominant (Ritchie *et al.*, 1985). Specifically, the accumulation of undecomposed organic matter in soil rich in biological remains of symbiotic microorganisms and their products, as well as the application of ammonia fertilizers with the consequent leaching of nitrates, are involved in the accelerated acidification of agricultural soils (Bolan and Hedley, 2003). Fertilization of agricultural areas, in addition to affecting the pH and CEC values of the soil, also affects the increase in the content of other elements in the

soil such as Cu and Zn, but other elements such as Pb, Cd, As, which belong to the group of heavy metals and can have a negative impact on the health of humans and animals that feed on plants grown on these lands (Atafar *et al.*, 2010).

### **THE INFLUENCE OF SOIL MECHANICAL COMPOSITION ON CATION EXCHANGE CAPACITY (CEC) VALUES**

It is well known that the content of clay minerals has a significant role in determining the physical, chemical and biological properties of the soil, but it also has a significant role in the formation of soil fertility potential, clay minerals as the smallest soil particles have a very important role in the adsorption and exchange of cations and anions with the soil solution, therefore it is of great importance to know the mineralogical composition of the soil and clay content in order to obtain a measure of soil fertility, determine the amount of necessary fertilizers and increase productivity (Hongling *et al.*, 2019). The assumption is that sandy soils (especially soils with a large proportion of coarse sand) have a low content of clay, organic matter, for this reason also a low value of cation exchange capacity (CEC), which particularly affects their physical, chemical and mineralogical properties, and therefore the possibility of agricultural production (Fidalski *et al.*, 2013). According to research (Soares and Alleoni, 2008; Adugna and Abegaz, 2015; Nešić *et al.*, 2015) the content of clay and organic matter affects the CEC of the soil, while research (Saidian *et al.*, 2016) made the opposite claim, indicating that the values CECs depend on the type of clay (smectite versus kaolinite) that was present in the soil, and not on the content of organic matter and the degree of its decomposition. Research (Hobley and Wilson, 2016) has shown that the mineralogical composition and the clay content in the soil have a great influence on the content of organic matter and its dynamics in the soil, and that pH-dependent charges play a significant role in increasing the CEC value in the soil associated with silanol and surface functional groups. Deprotonation of surface functional groups leads to the appearance of a negative charge, which leads to an increase in the cation exchange capacity (Sposito, 2008; Silva *et al.*, 2012). In this way, positively charged iron and aluminum oxides bind to negatively charged functional groups of soil organic matter, building organo-mineral complexes. These complexes depend exclusively on the accumulation of organic matter as well as on the ability of the soil system to change its surface charge (Souza *et al.*, 2020), thus preventing the mineralization of organic matter (Pishe *et al.*, 2011). The capacity for cation exchange is the most important chemical property of the soil and directly affects the loss of cations by leaching (Nešić *et al.*, 2015). CEC values did not show a significant correlation ( $p > 0.05$ ) with  $\text{Fe}_2\text{O}_3$  minerals, kaolinite. Kaolinite has a low CEC ( $\sim 1 \text{ cmol/kg}^{-1}$ ) of clay, while Fe oxides have very low CEC values in soils due to high pH ( $> 7.0$ ), (Sposito, 2008). Clay minerals having a ratio of 2:1 was also not correlated with different CEC values due to the combination of low concentration ( $< 50 \text{ g/kg}^{-1}$ ) and the presence of  $\text{Al}^{3+}$  ions in their interlayer which



neutralizes the permanent negative charge of these minerals (Azevedo and Torrado, 2009). When we analyze the total organic carbon (TOC) and expressed data through the C:N ratio, as well as the crystallized forms of Fe and Al and the free forms of Fe and Al favored the correlation since the values of these four properties are very small in sandy and loamy soils. In addition, poorly crystalline forms of Fe and Al oxides have a higher affinity for binding with soil organic matter than free forms of Fe and Al (Cornell and Schvertmann, 2003). The colloid complex of the soil consists of humus and clay, the most important acidoids that are able to create bonds between oppositely charged ions (cations) through forces strong enough to provide protection against leaching, and also weak enough to allow adsorption through the plant's roots. This ability becomes more pronounced if the degree of dispersion is higher, that is, if the particles have smaller diameters. Research results (Nešić *et al.*, 2015) for different types of soil in Vojvodina, such as chernozem, fluvisol, semigley, humogley, soloncak and solonjec, showed that the cation exchange capacity depends on the clay fraction and humus content. A higher correlation coefficient between CEC and clay, compared to CEC and humus, indicates that clay content has a greater effect than humus content on the cation exchange capacity, and the results of these studies are shown in Table 2.

Table 2. Average values of clay, humus and CEC content depending on soil type (Nešić *et al.*, 2015).

Soil type	Clay %	Humus %	CEC (cmol/kg)
Chernozem	19,44	3,05	22,72
Fluvisol	25,61	2,69	22,41
Semigley	23,04	3,45	31,99
Humogley	40,75	3,25	30,97
Soloncak	21,88	2,90	26,61
Solonjec	26,20	2,78	40,06
Average value	26,15	3,02	29,13

### INFLUENCE OF SOIL ORGANIC MATTER ON CATION EXCHANGE CAPACITY

The main source of organic matter in the soil is the remains of plants, animals and microorganisms, which are made of very complex organic substances such as: carbohydrates, proteins, fats, waxes, tannins, resins, pigments and organomineral complexes (Adugna and Abegaz, 2015). The importance of soil organic matter can perhaps best be described through the sentence that it represents the blood of the soil (Jungkunst, 2010). Its importance is also reflected in the characteristics that it serves as a reservoir of nutrients for plants by adsorbing nutrients, transforming them and protecting them from losses, which contributes to higher values of the capacity for cation exchange, and also affects the improvement of the physical properties of the soil, providing a medium for growth and the activity of microbes, significantly affects the buffering capacity of

the soil when applying acids and bases, which makes it less susceptible to changes in pH value, and also affects the release of organic acids during decomposition, which in the soil affect the processes of wear and transformation of rock minerals (Alhassan *et al.*, 2018; Tanimu and Liocks, 2013 and Totsche *et al.*, 2010). Studies on the effect of spatial variability of soil properties also indicate that soil organic matter and cation exchange capacity are strongly influenced by external factors such as agricultural production, soil management, as well as internal factors such as soil type and depth (Adugna and Abegaz, 2015). The content of organic matter characteristically decreases with increasing soil depth (Montes-Pulido *et al.*, 2017), while the capacity for cation exchange varies depending on the depth and type of soil and is also correlated with the amount of separated organic matter in an individual soil depth (Tomašić *et al.*, 2013). According to research (Topalović *et al.* 2022), organic matter enhances the olive tree productivity through positive effects on soil structure, water retention capacity and availability of some nutrients (limiting erosion, nitrogen leaching, phosphorus precipitation and iron inactivation). Soyergin *et al.* (2002) considered that the content of soil organic matter more than 1% being suitably for well growth. The level of total soil organic matter changes slowly and negative consequences for yield become visible only when the level of organic matter falls below 2% (Vojnov *et al.*, 2020b; Šeremešić *et al.* 2021b), which can result in an irreversible process of degradation of all soil properties. Given that soil OM is the main reservoir of soil organic carbon (SOC) (Schmidt *et al.*, 2011), it is necessary to investigate the fractions that are most prone to changes during land use (Ćirić, 2016; Šeremešić *et al.* 2020). Measuring and predicting the mechanisms responsible for soil organic matter conservation is very challenging due to the long periods required to detect changes, as well as the complexity of the physicochemical properties responsible for soil organic C stabilization (Van der Voort *et al.*, 2016; Harden *et al.*, 2018). In addition, the biotic activity of plants and microorganisms, as well as the physical and chemical properties of the soil, significantly influence the dynamics of organic matter in the soil (Torn *et al.*, 1997; Schmidt *et al.*, 2011; Doetterl *et al.*, 2015; Rasmussen *et al.*, 2018). A soil property used to determine variation in soil organic matter content and stability is percent clay (Coleman and Jenkinson, 1996; Wieder *et al.*, 2015). In principle, the clay content controls the stabilization of organic matter through the sorption of organic molecules on mineral surfaces <2 µm in size, as well as their occlusion into aggregates (Oades, 1988; Eusterhues *et al.*, 2003; Lutzov *et al.*, 2006). Structural soils were found to contain more organic matter than coarser textured soils (Rasmussen *et al.*, 2018). Although clay content for the purposes of assessing organic matter content is widely used in research due to ease of measurement, new research shows that this approach can simplify and inefficiently depict soil mechanisms that affect the preservation of organic matter (Bailey *et al.*, 2018; Rasmussen *et al.*, 2018). Clay minerals represent a class of minerals whose

surfaces come into contact with soil organic matter (Kaiser and Guggenberger, 2000; Vogel *et al.*, 2014). Research (Farrar and Coleman, 1967) suggests that the clay content does not provide sufficient information about the surface of the soil that can be available for the sorption of organic matter. Accordingly, other soil properties that affect the sorptive capacity of the soil can give a clearer picture of the mechanisms that affect the preservation and stabilization of organic matter in the soil (Bailey *et al.*, 2018). The sorptive capacity of soil surfaces represents the effective capacity for cation exchange (CEC ef.) and it represents the total amount of exchangeable cations that the soil can adsorb on its surfaces, at the pH value present in the field, at the low pH value present, mostly permanent charges of clay type 2:1 adsorb exchangeable cations, while at higher pH values positive ions are adsorbed on surfaces with variable charges such as 1:1 type clay minerals, allophane, organic matter and Fe and Al oxides (Weil and Brady, 2016). The effective capacity for cation exchange can represent a direct measure of the sorption of organic matter to adsorptive soil surfaces at existing pH conditions, whereby polyvalent metal cations such as  $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$  can play an important role in stabilizing organic matter, by binding organic compounds to mineral surfaces through exchangeable bridges and ionic bonds (Oades, 1988; Rasmussen *et al.*, 2018; Rowley *et al.*, 2018). Metal cations are of great importance in the binding of organic compounds in the soil, and the binding and stabilization of organic matter depends on the hydration shell and the valence of the cation, which is proven by chemical modeling that shows that bridges of exchangeable  $\text{Ca}^{2+}$  ions are more stable than bridges with exchangeable monovalent cations, because the radius ratio charging and hydration of  $\text{Ca}^{2+}$  ions enables a balanced repulsion between negatively charged particles in the soil (Sutton *et al.*, 2005; Iskrenova-Čukova *et al.*, 2010). The complexation of organic molecules with methane cations that are present on the surface of minerals through ionic bonds mainly refers to the displacement from the hydration shell of cations, the ionic potential, as well as the type of organic molecules present in the soil solution (Rowley *et al.*, 2018). In acidic soils, it was observed that the  $\text{Al}^{3+}$  ion plays a very important role in the complexation of organic compounds and the mineral surface, while the  $\text{Fe}^{3+}$  ion forms insoluble precipitates in the present pH conditions and is rarely found in the soil as a free ion, and the  $\text{Ca}^{2+}$  ion is weakly polarized and tends to form ionic bonds with ligands containing oxygen (O), such as carboxylic acids, and for this reason have the ability to form complexes with organic compounds (Sposito, 2008). Monovalent cations such as the  $\text{Na}^+$  ion do not form ionic bonds with organic ligands, while the  $\text{K}^+$  ion participates in complexes found in the interlayers of certain phyllosilicates (Rowley *et al.*, 2018). In addition to all of the above, metal cations can form organo-mineral complexes in the soil by linking several organic compounds together, which have been observed to cause aggregation and thus affect the physical protection of soil organic matter (Kunhi Mouvencheri *et al.*, 2012).

## PREDICTION OF CEC WITH PEDOTRANSFER FUNCTIONS

The soil pedotransfer function (PTFs) is used to obtain information on the most important soil properties, which are difficult to obtain (time or financially).

The pedotransfer function is defined as a statistical model for predicting physical (bulk mass, water-air regime, etc.) and chemical (cation exchange capacity) soil properties (Kumar and Gurung, 2002). Pedotransfer soil functions are also applied in soil studies to assess values that are difficult to measure in the field (Minasny and Hartemink, 2011). The soil pedotransfer function is obtained from available parameters from soil reserves, such as organic carbon and clay content. It is very important to get an equation that will show the parameters with certainty (Benites, 2007). The consistency of PTFs mainly depends on the number of samples and the range of input parameters (Chirico *et al.*, 2010). Pedotransfer functions for CEC are often developed from a combination of different properties such as clay content, organic matter content and hygroscopic water content (Arthur 2017; Krogh *et al.*, 2000; McBratney *et al.*, 2002; Olorunfemi *et al.*, 2016.). Research (Krogh *et al.* 2000) showed that PTFs based on clay and organic matter content in illite-dominated samples reliably explained 90% of CEC variability. Similar to research (McBratney *et al.* 2002), it was demonstrated that PTFs based on clay and OM content explained 73% of CEC variability. However, due to spatial variations in clay mineralogy and organic matter composition, it is necessary to develop different PTFs for different regions and soil types (Seybold *et al.* 2005). Regression and fuzzy logic are common methods used in PTF development (Ostvari *et al.* 2015a; Ostovari *et al.* 2019). In statistics, multiple linear regression (MLR) is a linear approach to modeling the relationship between a dependent variable and one or more independent variables (Herbst *et al.* 2002). The regression tree (RT) is a well-known method used in environmental science (Ostovari *et al.* 2019; Pachepsky and Rawls 2006; Pachepsky and Schaap 2004). This method represents data collection techniques that use qualitative and quantitative variables as independent variables. In the (RT) method, independent variables are introduced which are then selected by the software as effective variables (with high correlation) and divided into two groups according to the order of priority where by a tree-like structure is created, where in the first node there is a certain property that is divided into two groups/nodes by the variable that has the highest correlation with it. The best regression tree results when the variable chosen to create the greatest homogeneity in the new nodes is well correlated (Ostovari *et al.* 2019). In the research conducted by Keshavarzi, Sarmadian and Labbafi (2011), models were developed to predict CEC using MFIS and ANN, where data on clay content and % OM were used as variables in both systems. The results of that research showed that MFIS had a higher efficiency than ANN in predicting CEC. According to the research conducted by (Ostovari *et al.* 2015b) where the MFIS and RT method were compared in the estimation of CEC in the field, different soil properties including density, sand, dust and clay content were used as input variables in both methods, the results were showed that (RT) was more effective

than MFSI in estimating CEC. Assessment of CEC in soils in Semnana province (Iran) using ANN, MLR and fuzzy logic methods was performed on the basis of 200 soil samples, a regression model and non-specific rules were developed (Emamgolizadeh and Ghorbani, 2015). The results of these studies confirmed that the ANN method had better CEC prediction results than the MLR method and fuzzy logic. In separate studies conducted by (Ghorbani *et al.* 2015) and (Seyed-Mohammadi *et al.* 2016) where the ANN, MLR and fuzzy logic methods were compared, in the evaluation of CEC values, it was also found that the ANN method had better estimation results from MLR and fuzzy logic methods. In research conducted by (Nikseresht *et al.* 2019), a total of 100 soil samples collected across the USA were used, with the samples being divided into two groups, where 75 samples served as a calibration set for the MLR and RT models as well as to form fuzzy logic functions, the remaining 25 samples were used to validate the performance evaluation of MLR, RT and MFSI for the estimation of CEC values. For the development of PTFs using MLR, RT and MFSI methods, easily measurable soil properties such as soil particle size, organic matter content, volumetric mass, etc. were used. To begin with, the relationship between easily measurable soil properties and CEC was investigated, where the following linear equation  $CEC = aX + b$  as well as a non-linear equation in the form of  $CEC = a \log(X) + b$  was used for this purpose. Where X is an easily measurable property of the soil, a is the slope of the linear line and b is the intercept. The same easily measurable soil properties were used in the regression methods (MLR and RT) and were also used as input variables in the MFSI to predict CEC. To prevent multicollinearity given the high correlation between soil particle size ( $r=0.85$ , % clay with % dust and  $r=-0.064$  between % clay with % sand), the mean geometric diameter of the particles (dg) and the fractal dimension (D) obtained from soil particle size were applied to develop PTFs. These two values were calculated according to the proposed equations of Shirazi and Boersma (1984) and Sepaskhah and Tafteh (2013) as follows:

$$dg = \exp [ 0,1 ( P_{sa} * \ln(1,025) + P_{si} * \ln( 0,026) + P_{cl} * \ln(0,001) ) ]$$

$$D = 3 - 0,118 \left[ -\ln \frac{P_{cl}}{100} + \left( \frac{P_{si} + P_{sa}}{100} \right) \right]$$

where  $P_{sa}$ ,  $P_{si}$  and  $P_{cl}$  are % sand, % dust and % clay.

Research results (Nikseresht *et al.* 2019) showed that CEC has a positive significant correlation with % OM ( $r=0.68$ ;  $p<0.01$ ) and D ( $r=0.68$ ;  $p<0.01$ ). CEC also had a negative significant correlation with BD ( $r=-0.35$ ;  $p<0.05$ ) and dg ( $r=-0.52$ ;  $p<0.05$ ) Previous research conducted by (Ersahin *et al.* 2006) and (Baiat *et al.* 2014) also showed a positive correlation between CEC and D. In many previous studies conducted such as Keshavarzi, Sarmadian and Labbafi (2011), Shirani and Rafienejad (2011), and Memarian-Fard and Beigi (2009) and Ghorbani, Kashi, and Moghadas (2015), a highly significant correlation was

found between CEC content and OM. Research (Ostovari *et al.*, 2015) shows that in the range from 2.05 to 2.60 for D and 0% to 2% for OM, CEC has a minimum value, and with an increase in D and % OM, CEC values increase gradually. When it comes to soils with a high CaCO<sub>3</sub> content (carbonate soils), the assessment of CEC is difficult and expensive, although it can be measured by laboratory analysis (Carpena *et al.* 1972). There are various PTF models for estimating CEC values, related to basic physical and chemical soil characteristics, but PTF models that estimate CEC values on carbonate soils are poorly developed (Mahmoud *et al.* 2016, Khaledian *et al.* 2017). Research conducted by (Fattah *et al.* 2021) aimed to model PTFs that will predict CEC values in carbonate soils with high pH and low OM content, and for wide ranges in clay content, at for which they used statistical models based on different efficiency criteria (RMSE, AAPE, EF and PIME), whereby models were used:

$$RMSE = \sqrt{\frac{1}{(n-df)} \sum_{i=1}^n (O_i - P_i)^2}$$

$$AAPE = \frac{1}{n} \sum_{i=1}^n \left| \frac{O_i - P_i}{O_i} \right| 100$$

$$EF = 1 - \frac{\sum_{i=1}^n (O_i - P_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2}$$

where RMSE-root mean square error, AAPE-average absolute error in percentage and EF-efficiency coefficient of Nash-Sutcliffe model, O<sub>i</sub>-observed values, P<sub>i</sub>-predicted values, n-number of observations, O-mean value of observed values.

Research results (Fattah *et al.* 2021) showed that in carbonate soils with low OM content and high pH value, CEC values are related to the content of clay minerals, which are a source of negative charge.

## CONCLUSIONS

Knowing the value of CEC and humus content are the basis for the calculating required amount of fertilizers, while their monitoring can help in a prevention of nutrient leaching and ensure environmental protection. This study showed that although there are the trash holds and different level of CEC, this soil property has unique characteristics for single soil site. However, in many agronomic soil studies CEC has not received significant attention and recognition. In the future, soil analysis will benefit from accurate and extended data evaluation, as well as cost-effective models that can provide comprehensive insight between soil chemical, physical and microbiological properties. Given that CEC has a unique ability to encompass many soil properties knowing this value could help in defining cropping technology for stable yields and soil quality preservation. Therefore, farmers and practitioners should consider using CEC as a decision making tool that could be crucial for agricultural production in the future.

## ACKNOWLEDGEMENTS

This research was supported by the Ministry of education, science and technological development of the Republic of Serbia, within the framework of a contract on the realization and financing of scientific research work (project number: 451-03-47/2023-01/200117).

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