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Relations of Clay Fraction Mineralogy, Structure and Water Retention in Oxidic Latosols (Oxisols) from the Brazilian Cerrado Biome

Carla Eloize Carducci, Geraldo César de Oliveira, Nilton Curi, Eduardo da Costa Severiano and Walmes Marques Zeviani

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1. Introduction

In Brazil, Latosols are by far the main class of soils, mainly when one considers the soils potentially used for agricultural purposes. They cover approximately 50% of the Cerrado Biome, totaling about 200 million hectares, in [46, 52]. The clay mineralogy of these soils are very simple, basically composed by 1:1 clay minerals, mainly kaolinite, and varying proportions of iron- and aluminum-oxides (in this chapter this general term includes oxides, hydroxides and oxi-hydroxides). As the oxides content increases, they tend to be associated with the formation of granular structure, composed by very small and resistant micro-aggregates, occurring in both superficial and sub-superficial soil horizons.

To explain the formation of micro-aggregates in these highly weathered Latosols, in [30, 31] it is highlighted that iron- and mainly aluminum-oxides act as aggregating agents of mineral particles by changing the arrangement of their components in relation to the plasma, resulting in granular aggregates with a diameter < 300 μm, in an agglutinated pattern, having a high pore volume, which is in turn organized into interconnected cavities, in [100]. Consequently, in these soils, the pore distribution by size is predominantly characterized by two distinct classes of pores: the first one is related to very large or structural pores (among micro-aggregates), which promote rapid internal drainage of the soil, however, they are very susceptible to alteration; and the second one is related to very small pores or textural pores (inside micro-aggregates), in which water is retained with very high energy, in [10, 21, 63]. This segregation of contrasting pores is typical of oxidic Latosols from this region, in which the increase of clay content is associated with higher total porosity and lower bulk density, in [31, 37, 46, 72, 88, 89].

Thus, the content and nature of the clay fraction are very important in the hydro-physical behavior of these highly weathered soils. Under natural conditions, these soils have a high total pore volume, one part being composed by drainable pores (approximately 2/3 of the total pore volume; those with diameters > 145 μm), which are of fundamental importance for the soil high permeability. However, these soils also have high volume of pores with very small diameter (< 2.9 μm; approximately 1/3 of the total pore volume). Therefore, in order to remove the residual water content a considerable amount of energy is required, in [63]. Small amounts of water have been observed to be adsorbed on the soil matrix under 300.000 kPa pressure, in [10].

In the current stage of evolution of the agricultural systems in Brazil, in which yield increments are searched without increasing the productive area, it is necessary to understand in details the hydro-physical behavior of these Latosols, taking into consideration the environmental sustainability, in which underground water recharge is fundamental for the maintenance of the most varied types of edaphical life. It should be mentioned that irrigated agriculture in this region is undergoing accelerated growth and it is not clear until now if the existing water resources are sufficient to support this expansion, in [78]. These soils are usually very deep, providing large reservoirs of water for crops, since there are no chemical constraints for the expansion of the crop root system. Even in the sub-superficial soil horizons, the residual water plays an important role in the maintenance of adequate thermal and physical conditions, which minimizes root death during the pronounced dry season, which is typical of this region.

2. Cerrado biome, mineralogy and structure of Oxidic Latosols

The Brazilian Cerrado, which is the second largest biome in the country, is located in the central part of the South America, including large portions between parallels 3 ° and 24 ° south and between parallels 41º and 63º west. In Brazil, the biome occupies approximately 23.92% of the territory, covering several states (Mato Grosso, Mato Grosso do Sul, Rondônia, Tocantins, Minas Gerais, Bahia, Maranhão, Piauí, Sao Paulo, and particularly Goiás and the Federal District, where this vegetation covers the landscape on a relatively more continuous way (Figure 1), but there is still remaining "islands" of this biome in Pará, Roraima and Amapá states, in [5]. The soils that support this biome are hydrologically important since the major basins (Amazônica, Platina and Sanfranciscana) have many of their springs in this region, in [29, 47].

The Cerrado can be defined as a formation composed of tropical vegetation, represented mainly by grasses, with sparse trees and shrubs, in other words, including floristic and physiognomic aspects of vegetation, constituting a unique biome, in [29], also called neotropical savanna. The soils are represented by Latosols (Oxisols) (50%), Argisols (Ultisols) (15%), Quartzarenic Neosols (Entisols) (15%), Cambisols (Inceptisols) (10%) and Plinthosols (Oxisols having drainage restrictions) (6%) and other soils (4%), in [78]. The Latosols and Quartzarenic Neosols are located in predominantly gentle relief associated with a very sparse hydrography.

Figure 1. Cerrado area in Brazil, highlighting Goiás state and Federal District (darker area) (Source: [85])

The Latosols are considered the oldest soils on earth. They go from deep to very deep, non hydromorphic, and show great textural variation with clay content ranging from 150 g kg^{-1} to more than 800 g kg^{-1} [88, 89]; exhibit low natural fertility due to the strong weathering-leaching, which contrasts with their excellent physical conditions favored by the strong and very small granular structure. Latosols also tend to present high acidity (pH 4.0 to 5.5), low cation exchange capacity, high anion adsorption capacity (especially phosphate and heavy metals) and low levels of available P (phosphorus) to plants [27, 46, 77].

The beginning of weathering of Latosols in this region dates from the Cretaceous and Tertiary, in [54]. They were formed under conditions of significant weathering-leaching, which contributed to their advanced degree of pedogenic development, resulting in a very simple mineralogy, in [76]. Their clay mineralogy consists basically of 1:1 clay minerals, mainly kaolinite ($Si_2Al_2O_5(OH)_4$), iron oxides (hematite (Fe_2O_3) and goethite ($FeOOH$)) and aluminum oxides (gibbsite ($Al(OH)_3$)) in different proportions, as well as quartz and other resistant minerals, in [16, 38, 39, 44, 46, 54, 65, 73, 74, 75, 76, 77, 83]. There are also registers in the clay fraction of some Latosols formed from rocks richer in iron, of maghemite (Fe_2O_3) as well as magnetite (Fe_3O_4) and ilmenite ($FeTiO_3$) in the coarse fraction [93, 97]. The

identification of hydroxi-interlayered vermiculite in the clay fraction of A and B horizons of some Latosols has been also registered, in [71].

Knowledge of Latosol genesis facilitates the identification of their corresponding classes in international soil classification systems: the Oxisols in Soil Taxonomy, in [92] and the Ferralsols in World Reference Base [43]. As peculiar characteristics of Latosols can be cited: the presence of latossolic B horizon (Bw = intense weathering), minimal differentiation between A and B horizons, color varying from reddish to yellowish, depending on the parent material and the factors and processes of soil formation, in [15, 54]. They exhibit weak macrostructure and strong microstructure [28, 30, 31], resulting in 50-300 µm size micro-aggregates, in [100]. These soils constitute the largest class in terms of territorial expression having high potential for agriculture, forestry and livestock purposes, in [46].

The pelitic rocks of the Bambuí Group which occur in Minas Gerais, Bahia and Distrito Federal states are important parent materials of many Latosols of the Cerrado Biome. These rocks are fine grained, resulting in clayey or very clayey soils. In these soils, the kaolinite is the mineral with higher expression in the clay fraction, in [66] and its presence in combination with low levels of iron and aluminum oxides favors the hard consistency when the soil dries, and higher bulk density, which is related to the blocky macrostructure, function of the face-to-face arrangement of the kaolinite plates in [30, 31].

Ferreira et al., in [30] relating the mineralogy and structure of Latosols in southeastern Brazil, stratified them into kaolinitic or gibbsitic soils: in kaolinitic Latosols the micromorphological evaluation showed that the distribution of quartz grains in relation to the plasma, is porphyric. In other words, the grains are enveloped in a dense and continuous plasma, with little tendency to develop the microstructure. This phenomenon is associated with the blocky structure, so that the soils are more compact, less permeable, with lower aggregate stability in water and have a greater susceptibility to sheet erosion. On the other hand, the gibbsitic Latosols show a more uniform distribution of the minerals in relation to the plasma, resulting in smaller granular and resistant aggregates (< 300 µm diameter), in an agglutinated pattern, influencing higher void ratio, which are in turn arranged into interconnected cavities, in [100], showing a greater susceptibility to gully erosion.

Consequently, in these soils the pore distribution by size is characterized by presenting predominantly two distinct classes of pores: the first one is related to very large or structural pores (among micro-aggregates), which promote rapid internal drainage of the soil being, however, very susceptible to alteration; and the second one is related to the very small pores formed among the mineral particles (inside micro-aggregates), in which water is retained with very high energy, characterizing it as hygroscopic water, in [19, 21, 63]. This segregation of contrasting pores is typical of the oxidic Latosols from this region, in [73]. Usually, increasing the clay content of these oxidic Latosols results in increased total porosity and lower bulk density, in [30, 31, 89].

Based on this knowledge it can be understood that in very weathered tropical soils the micro-aggregates are very resistant and play a prominent role in the formulation of the soil aggregation hierarchy hypothesis. An indication of this resistance is the difficulty of evaluating the clay content in the field, requiring more time for reliable estimates, in [13]. This micro-aggregates resistance also manifests itself in the laboratory analysis of particle size distribution, mainly during the chemical and mechanical soil dispersion, in [38, 39, 63, 99].

3. Bimodal pore distribution and water retention of oxidic Latosols

The development of a specific type of soil structure is usually a consequence of the parent material and soil formation processes and factors, and these will condition many of the physical properties of soil. Marshall, in [55] stated the soil structure is defined as the arrangement of soil particles and the associated voids, including shape, size and arrangement of the aggregates formed by the primary particles (sand, silt and clay) which are grouped into units defined by limits. Marcos, in [53] cited that the morphological evaluation of the soil structure is qualitative, while the physical evaluation is functional.

It is known that soil macrostructure is strongly affected by climatic changes, biological activity, as well as the land use and soil tillage, being vulnerable to mechanical and physical-chemical forces, by according to Hillel, in [41]. In another words, composite structural units or aggregates are formed by aggregation of primary mineral particles in association with organic particles, especially the humidified ones, in [91], originating the soil structure, which influences the porosity. Thus, the aggregates have their own genesis reflected in their size, shape, composition and stability, in [9, 98].

According to with this soil structure model, there is a strong influence of the mineralogical components of the clay fraction upon formation of a particular structure type. It is reported, for instance, that oxides (mainly gibbsite, followed by iron oxides-goethite and hematite) jointly with organic matter, in this order of importance, tend to disorganize the particles at microscopic scale, in [30, 77].

Therefore, the higher content of these components has a greater degree of disorganization and, consequently, the structure tends to become of the granular type. So, gibbsite, iron oxides and organic matter are precursors and maintainers of the granular structure, which is typical of oxidic Latosols in the Cerrado Biome, and it results in high permeability values, in [30, 31].

In Latosols, the granular structure type is responsible for a lower bulk density and a higher porosity values compared to the blocky structure (kaolinitic Latosols), in [10, 22]. The developments of structural- or among micro-pores (> 50 μm diameter) are more expressive in oxidic Latosols, followed by textural- or inside -micro-pores (< 50 μm diameter), in [14, 50, 63]. In oxidic Latosols, the structural pores exhibit a relationship with clay content reflecting on their hydro-physical attributes such as water retention. This feature can be considered a special characteristic of oxidic Latosols, in [31, 86-89].

Therefore, the presence of this type of structure formed by stable micro-aggregates, especially in the Bw horizons of oxidic Latosols, consequently determines the dominance of structural porosity over textural porosity, giving to these soils excellent permeability and moderate to low water retention, in [14].

The voids of the soil are formed by various processes that result in different pore shapes and sizes that affect the soil functions. For instance, the water and gases transportation occurs through the interconnected pores. The soil structure is considered to have various hierarchical levels, namely: a) groups of primary particles which comprise micro-aggregates; b) groups of micro-aggregates comprising aggregates; and c) groups of aggregates comprising much larger aggregates or soil clumps, in [19].

The pore distribution by size affects the soil hydro-physical dynamics. In the literature there are several classification schemes for pore diameter, highlighting the most simplified ones that separate two classes of pores: macro-pores, when the pores have a diameter > 50 μm, and micro-pores, when the pores have a diameter < 50 μm, as proposed by Kiehl, in [49] and Richards, in [79]. Pores of intermediate size, meso-pores, have lower expression in the Latosols from the Cerrado Biome, in [10].

There are equations that aim to quantify the pore size. Bouma, in [6] proposed the following equation: $D = 4\sigma \cos \theta / \Psi_m$, being: D = pore diameter (mm), σ = water surface tension (73.43 kPa at 20 °C); θ = contact angle between the meniscus and the wall of the capillary tube (assumed to be 0) e Ψ_m = matric potential (kPa). However, there are simple and straightforward methods to determine the pore size distribution, for example, using mathematical models to describe the water retention curve, because it is known that the shape and slope of the curve correspond to the homogeneity of the distribution of pore diameter, in [2, 19, 36].

Thus, the bimodal pore distribution of oxidic Latosols can be represented from the water retention curve, in [10]. When using the shape of the curve, the first inflection point occurs at low matric potentials (between 1 and 3 kPa, in absolute value) identifying structural pores, while the textural pores are represented by the second inflection point that occurs at extremely high matric potentials (between 10.000 and 20.000 kPa). Between these maximum points it can be observed that the asymptotes, related to the presence of intermediate pores, have low expression in oxidic Latosols in [10, 21, 22, 75]. In soils of temperate regions, the bimodality has been observed within the range of the standard curve of water retention, in the range from 1 to 1.500 kPa in [21, 22] due to the more uniform pore distribution, compared to soils of tropical regions.

It is noteworthy to remember that the soil water retention depends on pore distribution, and this is influenced by various factors such as structure, particle size distribution, organic matter, clay mineralogy, as well as biological activity. There are two possible reasons for the influence of mineralogy on the soil water retention: a) specific surface area; and b) presence of electrical charge of clay minerals. The larger the specific surface area and the higher the electrical charge is, the more water can be bound to the clay minerals, in [62, 34].

Thus, there is a substantial process of water being adsorbed on the surface of clay minerals by electrostatic forces and, hence, the water retention. Gaiser et al. [35] observed significant differences in soil water retention with different mineralogy, noting that soils with low activity clays (1:1 clay minerals and iron- and aluminum-oxides) retain less water when compared to soils that have high activity clays (2:1 clay minerals), using pedotransfer functions. Several studies have indicated a strong influence of clay fraction on water retention in Latosols, in [1, 4, 10, 11, 70, 73, 89]. A few authors claim that clayey Latosols having oxidic mineralogy favor higher water content and more gradual decrease of soil water content with increasing matric potential (in absolute value). The study of water retention developed by van den Berg et al., in [96] in Latosols from different regions showed that the increased release of water occurs at low potentials (between 5 and 10 kPa) similar to what happens with very sandy soils. The spatial variability of water retention in clayey Latosols was studied by Cichota & van Lier, in [12]. These authors observed that the water retained at matric potentials ranging from 1 to 100 kPa is not strictly related to the content of clay, which confirms the theory of Raws et al., in [70] that at low matric potentials the retention curve is directly influenced by structure stability and consequently by the formation of pores in addition to the indirect effects of organic matter.

Many advances have been made in order to better characterize soil water retention. More sophisticated devices as the WP4-T, in [18] should be highlighted, which allows the quantification of the residual water retained at high matric potentials. The residual water retained in the textural pores of oxidic Latosols, although considered unavailable to crops, in [50, 80], may reflect significant water content (up to 0.25 g g^{-1}) in more clayey soils, in [10]. So, it becomes of great interest in studies involving regulation of microbial and biochemical processes in the soil, in [60], re-induction of desiccation tolerance of germinating seeds and seedlings when subjected to high matric potentials ($\Psi_m > 1.500$ kPa), in [81] and it can act as a lubricant between aggregates, when the soil undergoes external pressure during mechanized operations in [23].

4. Modeling the water retention curve of oxidic Latosols

Water retention curve has been used to describe the dynamics of the soil water, in [20, 36]. This curve graphically represents the relationship between the energy of water retention (matric potential, in logarithmic scale) and water content, which is dependent on the intrinsic characteristics of each soil, the result of joint action of soil attributes such as texture, structure, mineralogy and organic carbon, in [4, 19, 37, 40].

Several types of adjustments to the water retention curve have been used, in [25, 36] for describing the soil hydro-physical performance. However, in order to identify the bimodal distribution of pores in oxidic Latosols the double van Genuchten model was recently proposed by Carducci et al., in [10]. Based upon the shape of the curve, the first inflection point usually occurs at low matric potentials, representing the structural pores, while the textural pores are represented by the second inflection point that occurs at higher matric potentials. For soils from temperate regions, the bimodality of pore distribution has been

observed within the range of the standard curve of soil water retention, in other words, in the range from 1 to 1.500 kPa (in absolute value), in [22] because there is a more uniform distribution of pores, when compared to soils from tropical regions. This mathematical model allows to identify, with high predictive power, the bimodal density function for the pore size distribution of tropical soils in a more superior range than to the one of the standard curve: $1 < \Psi_m < 300.000$ kPa).

One purpose of science is to find, describe and predict the possible relationships between events occurring in the environment. A common practice is to develop models that relate these events. For this purpose, statistical modeling is widely used, mainly by the use of linear and nonlinear regression models, in [56]. The two classes of regression models differ mainly in aspects related to their application and the characteristics linked to the mathematical form. The choice of which model to consider in fitting a certain set of data can be made intuitively, or through a graphical which expresses the function of the variables or prior knowledge of the phenomenon in question.

The linear models are widely used for presenting analytical solution for estimating parameters and statistical properties. The interpretation of these parameters is purely mathematical, based on rate of variation of the dependent variable in relation to the independent variables, in [94]. Furthermore, the use of a linear model for predicting values outside the range of observed values of independent variables is not advisable. Although the linear model is very flexible, since many models can be formulated by the combination of independent variables, in [26], there are several types of models which are based on theoretical considerations inherent to the phenomenon which one has interest in knowing, i.e., the called mechanistic models, in [56, 84]. Generally in these models the parameters have practical interpretation and the prediction of values is allowed, since when considering the mechanistic model the restrictions which ensure the model utility are imposed, in [3].

A model is considered nonlinear when the mathematical expectation of a dependent variable "Y" cannot be written as a linear function of parameters in a regression model. Historically, nonlinear regression models date from early 1920's, in [33]. However, the application and a detailed investigation of these models had to wait for the advancements allowed by computational calculations after 1970, in [24].

The rise up of nonlinear models often accompanies the forecasts involving physical and/or biological dynamics about the phenomenon under study in [102]. Such expectations are based upon models in which the parameters have practical significance in describing the phenomenon that is observed.

The function of statistics in this scenario is to evaluate, select, and provide models and tools for better understanding of these phenomena. An overview of a nonlinear model considers a set of p columns of a matrix X and a vector of parameters $\theta = (\theta_1,...,\theta_k)^T$ such that the average related to a response Y is given by:

$$E(Y|X = x) = f(x, \theta) \tag{1}$$

Where f is the function average or expectation of Y. Unlike linear models, the numbers of columns of the matrix X does not necessarily need to be equal to the number of parameters in the vector θ. Many of the functions impose restrictions on parameters (eg: $\theta_i > 0$, i = 1,...,k) due to both practical interpretations of the compatibility of mathematical relationships. The variance of Y in turn is given by:

$$Var (Y|X = x_i) = \sigma^2 \tag{2}$$

The above equations, including the presupposition of independence between observations, define the classic nonlinear model. The only difference between the classes of models is the form of the expectation function. The function is nonlinear regarding the parameters, and therefore, many parallels can be drawn regarding the procedures for estimation of parameters and statistical inference. The fitting of nonlinear models can be obtained by minimizing the residual sum of squares, $RSS(\theta)$, where:

$$RSS(\theta) = \sum_{i=1}^{n} \left(y_i - f(x_i, \theta) \right)^2 \tag{3}$$

By inspection of all values from the parameter space of $\theta \in \Theta$.

For linear models there is an analytical solution for the estimating $\hat{\theta}$ that minimizes $RSS(\theta)$. For nonlinear models the search for the minimum point of equation (3) is usually a problem with the numerical solution. Such problem uses a linear approximation of nonlinear function that converges to the minimum point at each iteration, in [48]. This procedure, as expected, also provides rough estimates for standard errors and hypothesis tests, and such approach is a function of how strong the nonlinearity of the model.

The Taylor series approximation of the function of expectation around a value θ^* considering expanding to the second term, can be written as:

$$f(\theta) \cong f(\theta^*) + F(\theta^*)(\theta - \theta^*) + \frac{1}{2}(\theta - \theta^*)^T H(\theta^*)(\theta - \theta^*) \tag{4}$$

Where F (θ^*) and H (θ^*) are the score matrix and hessian arrangement, respectively. The j-th column vector of the score matrix is given by $\partial f(x, \theta) = \partial \theta_j$ and the jl-th column vector of the hessian matrix is given by $\partial^2 f(x, \theta) = \partial \theta_j \partial \theta_l$, both evaluated at $\theta = \theta^*$.

Omitting the second term of the expansion (4), we can rewrite (3) as:

$$RSS(\theta) \cong \sum_{i=1}^{n} \left(yi - f(xi, \theta^*) - F(\theta^*)(\theta - \theta^*) \right)^2$$
$$\cong \sum_{i=1}^{n} (\hat{e}_i^* - F(\theta^*)(\theta) - (\theta^*))^2 \tag{5}$$

$\hat{e}_i^*$ is the current residuum that depends on the current value of θ^* in the iterative process. In the re-writing of the matrix form, the minimization process can be written as:

$$\widehat{\theta - \theta^*} \cong [F(\theta^*)^T F(\theta^*)]^{-1} F(\theta^*)^T \hat{e}^*$$
$$\hat{\theta} \cong \theta^* + [F(\theta^*)^T F(\theta^*)]^{-1} F(\theta^*)^T \hat{e}^* \qquad (6)$$

The equations (6), below, are applied in two forms: first to support the algorithm for the estimation of θ and the second as the basis for statistical inference on the parameter estimates, in [48]. The majority of statistical packages use the Gauss-Newton algorithm to find the parameter estimates in nonlinear models. Other packages also present derivative forms or algorithms based on other optimization processes. Practically algorithms differ at execution time. However, the efficiency of any one of them is very dependent on the value $\theta^{(0)}$ and $\hat{\theta}$ given at the beginning of iterative process. Depending on the numerical distance between $\theta^{(0)}$ and the algorithm can converge to a local minimum, or even not converge, therefore, suitable choices for $\theta^{(0)}$ in this sense are more important than the iterative method.

At each iteration the algorithms gets closer to the θ value which minimizes the sum of squared residuals, and hence $\hat{e}^*$ increasingly approaches the final residue. In this process one can think that $\hat{\theta}$ is equal to the parametric value plus a linear combination of random variables (e), so by the limit central theorem and satisfying certain regularity conditions, $\hat{\theta}$ will present approximately normal distribution, in [84]:

$$\hat{\theta} \sim N(\theta, \sigma^2[F(\theta)^T F(\theta)]^{-1}) \qquad (7)$$

An estimate of the variance is obtained by replacing in θ by $\hat{\theta}$ in equation (7),

$$\widehat{Var}(\hat{\theta}) = \hat{\sigma}^2 \left[F(\hat{\theta})^T F(\hat{\theta}) \right]^{-1} \qquad (8)$$

In which the second estimate σ^2 is:

$$\hat{\sigma}^2 = \frac{RSS(\hat{\theta})}{n-k} \qquad (9)$$

Where k is the number of estimated parameters of the expectation function and n is the sample size.

These results are generalizations of those obtained in linear models, and hence, the inferential methods such as F test for comparison of corresponding models, t for testing hypotheses about the parameters, can be applied to nonlinear models. These tests are simple extensions of the applied ones to linear models that are submitted to an appropriate linear approximation. Due to this, in contrast to the linear case where the same hypothesis is inspected similarly by different procedures with the same descriptive level, in nonlinear models equivalent tests may lead to differing conclusions. For instance, the Wald test for H_0: $A\theta = d$ may not produce the same result by the F test of model reduction, in [26]. The properties of these tests depend both on the sample size and the intensity of nonlinearity of the model.

Once obtained the estimate of the parameters it is possible to establish the asymptotic standard error for expectation E(Y) at a given point x_i:

$$ase\left(f\left(x_i,\hat{\theta}\right)\right) = \sqrt{\hat{\sigma}^2\,\hat{F}_i\left(\hat{F}^T\hat{F}\right)^{-1}\hat{F}_i^{\,T}} \tag{10}$$

Where is $\hat{F}_i$ is an abbreviated representation of $\hat{F}$ (x_i; $\hat{\theta}$).

An confidence interval of $(1 - \alpha)$ to covering E (Y) in a given association x_i can be obtained by:

$$f\left(x_i,\hat{\theta}\right) \pm t_{\alpha/2,n-k}\,ase\left(f\left(x_i,\hat{\theta}\right)\right) \tag{11}$$

As discussed above, one can see that all inference procedures for nonlinear models admit supposition of adequate linear approximation and make use of asymptotic arguments.

With the method of generalized nonlinear least squares it is possible to model the heterogeneity of variance in a specification similar to that used to model the response variable average. Davidian & Giltinan, in [17] presented the following expressions for the general definition of the variance function:

$$Var(y_i) = \sigma^2 g^2(\mu_i, x_i, \delta), \mu_i = f(x_i, \theta) \tag{12}$$

The variance of the response in equation (12) is a function $g(\cdot)$, which in turn may be a function of the response average (μ) of the fixed effect of independent variables (x) and of the parameter vector (δ) associated with the variance function $g(\cdot)$. Not necessarily g($\cdot$) must be specified as a function of all arguments. The variance function can be represented by any continuous positive function, being the most common are the exponential function and power function:

$$g(\mu_i, x_i, \delta) = exp(\delta\mu_i)$$

$$g(\mu_i, x_i, \delta) = |\mu_i|^\delta \tag{13}$$

The process of estimating the variance function is based on generalized least squares. Following the estimative parameter δ and choice of initial values for θ, an iterative process to generates definitive values for the parameters by minimization of the pseudo-verisimilitude function with respect to θ:

$$PV\left(\theta^{(0)}, \sigma, \delta\right) = \sum_{i=1}^{n}\left(\frac{\{y_i - f(x_i, \hat{\theta}^{(0)})\}^2}{\sigma^2 g^2(f(x_i, \hat{\theta}^{(0)}), x_i, \delta)} + log\left(\sigma^2 g^2\left(f\left(x_i, \hat{\theta}^{(0)}\right), x_i, \delta\right)\right)\right) \tag{14}$$

Technically, the above minimization means the verisimilitude maximization in relation to θ. For minimization of the above expression, by iteration, it is necessary the knowledge of θ. Regardless of the variance and $g(\cdot)$ function, minimization of the equation implicates on minimization of the sum of squares errors ($\{y_i\text{-}f (x_i; \hat{\theta})\}^2$). However, the most suitable the estimated variance values and of the $g(\cdot)$ function, smaller the sum squared errors. Computationally, the algorithm employed provides the joint estimation of the θ, σ^2 and δ parameters.

The heterogeneity of variance is corrected by specifying the variance function and estimates the associated parameters. Therefore, those observations that have larger deviation have their influence on the estimation of parameters ponderated by its variance. The standard errors of the parameter estimatives at the end of the estimation procedure are considering only the variance due to residual error, free of the difference in dispersion observed for the response variable.

Based on concepts of nonlinear models mentioned above, there are applications of these in various areas of Soil Science. As plausible examples it can be mentioned nonlinear regression models to predict soil nitrogen mineralization, in [67, 68] models of potassium release from various sources of organic residue in Latosol, in [101] extraction of zinc from sewage sludge, in [95] as well as the nonlinear model of Genuchten, in [36] which is the most used worldwide to describe the soil water retention.

The soil water retention curve is a nonlinear theoretical model which relates to water content with the matric potential. This feature is specific for each soil, in [4] being that the water content held in a given Ψ_m depends on the structure, the pore distribution and bulk density in which capillary phenomena are of greater importance. However, when the adsorption phenomenon governs, it is dependent on the texture and specific surface area of the mineral particles of clay fraction, in [1, 4, 41, 70].

Its graphic representation is based on the survey of a certain number of points, usually selected arbitrarily, by plotting the abscissa axis the logarithm of matric potential ($\log \Psi_m$) and on the ordinates axis the soil water content (U, g g^{-1}, θ, dm^3 dm^{-3}). Based on these points, a curve is delineated to represent the soil water retention characteristics.

The knowledge of the water retention curve has practical and scientific applications, including: determining the inflection point as being the field capacity, in [20, 32, 57,58] the slope of retention curve at the inflection point, in another words, obtaining the physical parameter "S", in [19] total water availability and drainable porosity, in [57], water content and pore size distribution, in [63, 50] non saturated hydraulic conductivity, in [36, 103] among others.

Several nonlinear models are used to describe the relation between water content and matric potential, in [2, 7, 8, 19, 36, 42, 45, 57, 58, 61, 82]. These empirical models continue to be used in order to adjust the soil water retention curves because it has not been developed theoretical mathematical expressions capable of adequately represent this physical-hydrical relationship. In adjusting the water retention curve is expected that the greater the number of points, the better representation of the soil water retention in [90].

At low matric potentials, the retention curve is directly influenced by the stability of the structure and, consequently, by the formation of structural pores in addition to the indirect effects of organic matter, in [64, 72]. In high matric potentials, the water retention is influenced by textural pores associated with particle size distribution and soil mineralogy, becoming the more important due to the available surface for water

adsorption, in [51]. This relation between the factors mentioned above characterizes the non-increasing monotonic function, which is common to all mathematical models of the water retention curve.

For the soil physical-hydrical description, the theoretical model proposed by Genuchten, in [36] has been universally adopted and allows to relate, with high predictive power, the retention energy and the water availability, in [19]. This model is characterized by two asymptotes, related to soil water content corresponding to saturation and the residual content, and an inflection point between the plateaus, which is dependent on soil properties, being its shape and its slope regulated by empirical parameters of adjusting of the model ("α", "n" and "m"). The estimative of the water retention curve is given by fitting the tested model to the data from the undisturbed soil samples, submitted to the interval of the standard matric potential (1 at 1.500 kPa).

Despite its extensive use in relation to other available models, in [25] it does not adequately fit to soils with bimodal distribution of pores, i.e., soils with two contrasting classes of pores, classified into structural and textural pores, in [22]. As a result, modelings have been proposed which employ equations capable of identifying this distribution, in which these pore classes are quantified by means of two maximum points, obtained by derivation of the water retention curve, in [2, 19] and consequently, two inflection points.
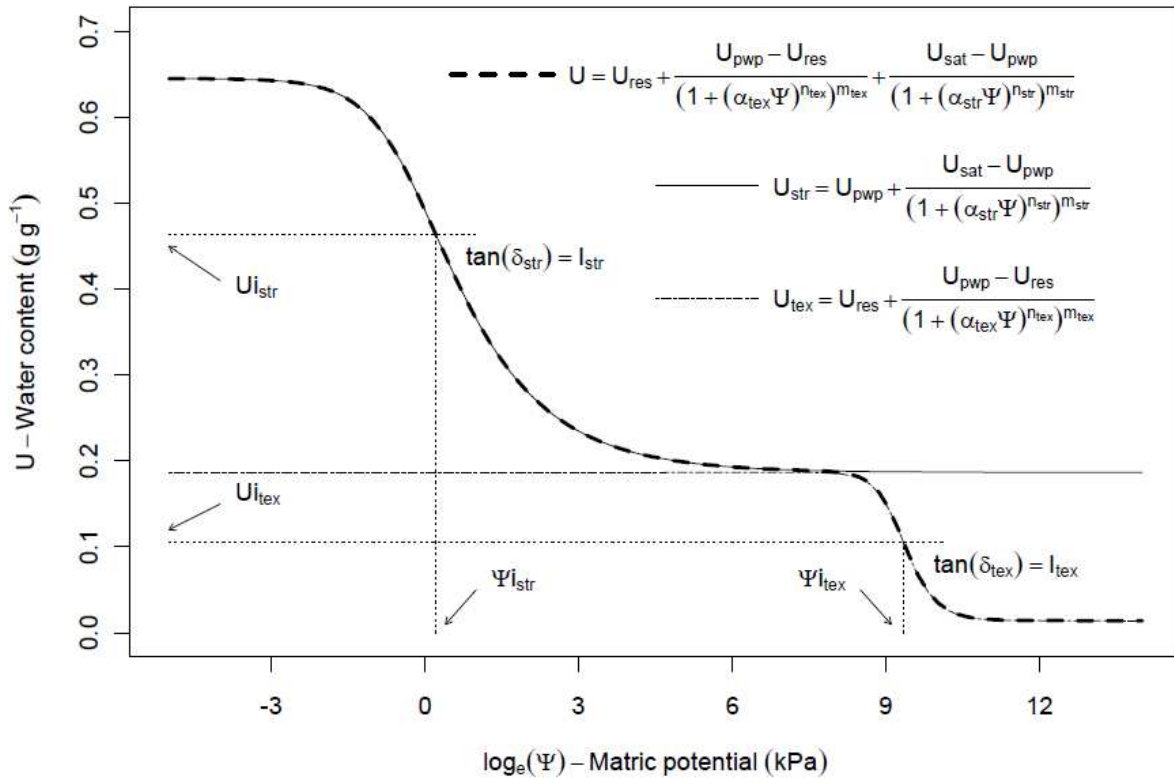
The double exponential model proposed by Dexter et al, in [19] allows identifying the bimodal pore distribution in soils from temperate region in the matric potential interval related to the saturation water content (U_{sat}) up to the residual water content (U_{res}). On the other hand, the Alfaro Soto et al. model, in [2] identifies the bimodal pores distribution in tropical soils in a matric potential interval upper to the standard determination ($1 < \Psi_m < 100.000$kPa) of the water retention curve.

The application of theoretical models, both in unimodal- and bimodal-pore distribution soils, provides only the description of the water content average value as a function of the matric potential and does not consider the possible correlation attributable to observed measurements in the sample at different matric potentials. In addition, these models do not consider the heterogeneity of variance, which was studied by Moraes et al, in [59] which found reduction of dispersion of the water content by increasing the matric potential.

A new model of adjustment for the water retention curve was proposed, in [10], denominated double van Genuchten (Figure 2). So, as well as other models, in [2, 19] the derivative of this model presents the bimodal density function for the pore size distribution of soil tropical, which stratifies the porosity of these soils into structural and textural pores, obtained by two inflection points which are evident from the nonlinear relation among the variables, expressed by this model, considering, however, the different matric potential interval for establishment of water retention curve ($1 < \Psi_m < 300.000$ kPa). However, due to the higher number of parameters, the template double van Genuchten becomes more flexible.

The equation below (Figure 2) shows m=1-1/n restriction, in [61] for both curve segments, structural (m_{str}) and textural (m_{tex}). The gravimetric water content and matric potential are represented by U and Ψ, respectively. The parameters U_{res}, U_{pwp}, U_{sat} represent the inferior asymptotic plateau ($\Psi \to \infty$) or asymptotic residual water content, the intermediate plateau, represent the value of water content which is slightly constant around the permanent wilting point and the upper asymptotic plateau ($\Psi \to 0$), indicates the saturation water content, respectively. The α and n parameters are associated with the scale and shape of the curve between top, middle and bottom asymptotes; α_{str} and n_{str} (structural) correspond to the first segment and α_{tex} and n_{tex} (texture) to the second segment of the curve. This procedure of adjusting of nonlinear models can be obtained by employing the 2.14.1software R, in [69].

$$U = U_{res} + \frac{U_{pwp} - U_{res}}{\left(1 + (\alpha_{tex}\Psi)^{n_{tex}}\right)^{m_{tex}}} + \frac{U_{sat} - U_{pwp}}{\left(1 + (\alpha_{str}\Psi)^{n_{str}}\right)^{m_{str}}}$$

$$U_{str} = U_{pwp} + \frac{U_{sat} - U_{pwp}}{\left(1 + (\alpha_{str}\Psi)^{n_{str}}\right)^{m_{str}}}$$

$$U_{tex} = U_{res} + \frac{U_{pwp} - U_{res}}{\left(1 + (\alpha_{tex}\Psi)^{n_{tex}}\right)^{m_{tex}}}$$

Figure 2. Proposed model for adjustment of the double van Genuchten function for retention curve, with the locations of parameters associated with the model, being matric potential (Ψ) and water content (U) estimated from the first inflection point (I_{str}) and the second inflection point (I_{tex}), in [10]

On the other hand, the water retention curve represents a cumulative distribution, thus, its derivative is proportional to the probability density function, and this function represents the distribution density of pores by size. The slopes represent the class of pore diameter that occurs most frequently. It explains why a larger quantity of water is removed when it is applied a tension corresponding to that diameter of the pores and therefore there is a great loss of water around this matric potential. The double van Genuchten model generalizes this assumption to accommodate the bimodal pore distribution, and therefore, the function has two inflection points.

5. Final remarks

A higher content of iron- and aluminum- oxides in the clay fraction of clayey Latosols (Oxisols), widely dominant soils in the plateaus of the Brazilian Cerrado Biome, currently the most demanded for sustainable grain production, is associated with the soil granular structure of these oxidic soils. This structure, when well expressed as in the B horizon of these very old Latosols, favors in the soil the existence of two distinct populations of pores: the bigger pores or structural pores (among aggregates) and the smaller pores or textural pores formed between the mineral particles (inside aggregates). This means that in these soils practically there are no pores between these two limits. This condition is also valid for sandy soils.

In this context, the model recently proposed by Carducci et al, in [10], and much detailed in this chapter adequately contemplates this bimodal distribution of pore size and functionality with respect to soil water retention in these peculiar soils in this important Brazilian Biome (one of the last agricultural frontiers in the world).

This represents a conceptual and methodological advance and an adapted modeling to the mineralogical and structural characteristics of these soils, in a region characterized by well-defined wet and dry season, with direct consequences on the water dynamics in these soils and in the environment in general.

Author details

Carla Eloize Carducci, Geraldo César de Oliveira and Nilton Curi
Department of Soil Science, Federal University of Lavras, Brazil

Eduardo da Costa Severiano
Federal Institute of Education, Science and Technology of Goiás State, Brazil

Walmes Marques Zeviani
Department of Statistics, Federal University of Paraná, Brazil

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