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Hassan Al Majou[a,b], Fabrice Muller[a, c], Philippe Penhoud[a], Ary Bruand[a]

[a]Université d'Orléans, CNRS, BRGM. Institut des Sciences de la Terre d'Orléans (ISTO), UMR 7327, 1A rue de la Férollerie, CS 20066, 45071 Orléans Cedex 2, France ; [b]University of Damas, Department of Soil Science, Faculty of Agronomy, PO Box 30621, Syria ; [c]Université d'Orléans, CNRS, Interfaces, Confinement, Matériaux et Nanostructures (ICMN), UMR 7374, 1B, rue de la Férollerie, CS 40059, 45071 Orléans Cedex 2, France.

Corresponding author: Ary.Bruand@univ-orleans.fr, Tel: 33(0)238492534, Fax: 33(0)238494476, Université d'Orléans, CNRS, BRGM. Institut des Sciences de la Terre d'Orléans (ISTO), 1A rue de la Férollerie, CS 20066, 45071 Orléans Cedex 2, France

ABSTRACT

Studies on clayey soils developed in temperate areas have shown that their water retention properties are related to both the clay content and the specific pore volume of the clay, the latter being related to the hydric history of the soil. Our objective was to discuss the validity of these results for clayey soils developed in semi-arid areas. Samples were collected in soils located in Syria. Physico-chemical properties were determined. Water content was measured at field capacity and for water potentials ranging from –10 to –15000 hPa. X-ray diffraction analyses were performed on the clay fraction to identify the clay. Results showed that the clays have both a high cation exchange capacity (0.707 to 0.891 mmol+ per g of clay) and a high external specific surface area (112 and 178 m² per g of clay).

These values are consistent with the X-ray diffraction results which showed the presence of a high proportion of smectite in most horizons and secondarily of varying proportions of illite and chlorite; kaolinite, while present, was not abundant. Results also showed that the amount of water retained by the clay according to the water potential was closely related to the specific pore volume of the clay at field capacity. Regression equations established by using both the data published earlier and those of this study enabled us to predict the water retention properties of clayey soils for a larger range of clay mineralogy and climatic environments including semi-arid environments than previously discussed in the literature.

Keywords: Clay content, Bulk density, Cation exchange capacity, Specific surface area, X-ray diffraction, Pedotransfer function.

Introduction

Clayey soils are often intensively cultivated in semi-arid and arid areas, particularly when irrigation is available (e.g., Ethan & Umar 2001; Mason et al., 2015). Their physical properties are closely related to the clay content and clay characteristics such as their mineralogical nature, the size of the elementary clay particles and the nature of the exchangeable cations (Tessier & Pédro 1987; Quirk 1994; Wilson 1999; Churchman & Velde 2019). Whatever the soil texture and more markedly in semi-arid and arid areas, it is important to ascertain the water retention properties of soils in order to manage the water supply and consequently crop growth appropriately (Gaiser et al., 2000). To accomplish this, pedotransfer functions that enable prediction of the water retention properties of soils have therefore been developed (e.g., Bouma & Van Lanen 1987; Wösten et al., 1999; Al Majou et al., 2008a & 2008b; Ostovari et al., 2015; Kalumba et al., 2020; Singh et al., 2020; Xu Xu et al., 2021), with several studies focusing on soils of semi-arid and arid areas (Tóth et al., 2012; Khlosi et al., 2012 & 2016; Al Majou et al., 2018; De Paepe et al., 2018; Santra et al., 2018; Dharumarajan et al., 2019; Soleimani et

al., 2020). At the same time, some studies aimed at a better understanding of the water retention properties of soils according to the characteristics of their clay minerals but the validity of the results for soils of semi-arid and arid areas remains unclear (Gaiser et al., 2000; Moret-Fernandez et al., 2013). For clayey soils developed on sedimentary materials, Bruand and Tessier (2000) showed that relationships between water retention properties and clay particles characteristics can be established. The clay particles, thanks to their fine size (< 2μm), play a privileged role in water retention and soil structuring but also in the retention and bioavailability of chemical elements essential for plants (Bergaya & Lagaly 2013; Churchman & Velde 2019). Depending on the characteristics of clay particles, i.e. both their size and shape, the nature of the cations in the interlayer space and on the external surfaces, the clay fabric, which corresponds to both the volume of clay particles and the associated pore volume resulting from their assemblage, can vary highly from one soil to another, with significant consequences for the water retention properties of the soil (Tessier et al., 1992; Bruand & Tessier, 2000; Boivin et al., 2004). However, most studies on the water retention properties of clayey soils were developed for clayey soils in temperate areas and their validity for clayey soils in other climate areas is still under discussion. D'Angelo et al. (2014) studied the high sensitivity to drought of Chinese red clay soils developed on clayey sediments in humid subtropical areas. They showed that it was related to a very dense clay fabric which resulted from a high degree of consolidation, leading to a small porosity able to retain water available for plants. Other clayey soils in tropical and subtropical areas exhibit a strong micro-granular structure and their water retention properties are closely related to both inter- and intra-microgranular porosity (Balbino et al., 2004; Tawornpruek et al., 2005; Reatto et al., 2007). In this study, the objective was to analyze the water retention properties of clayey soils developed in semi-arid areas of Syria and to show how results recorded in earlier work on soils located in temperate areas (Bruand & Zimmer, 1992; Bruand & Tessier, 2000; Al Majou et al., 2008a) can be applied to the soils studied. We discuss how both the clay content and pore volume developed by the clay fabric, the latter being related to clay mineralogy and size of the elementary clay particles as well as the hydric history, can be used to predict the water retention properties of the clayey soils studied.

Materials and methods

The soils studied

The soils studied are located in semi-arid areas of Syria (Rigot 2006) between latitudes 32 and 41° N and longitudes 35 to 42° E. A set of 10 samples (clay content > 0.3 g g^{-1}) including 4 horizons A and 6 horizons B were collected in 5 clayey soils located in the vicinity of the towns of Jabah (JB 1 and JB 2), Al-Suwayda (SW 1), Al-Tha'Ala (TH 1) and Al-Qamishli (QM 1) (Table 1). The soils developed on clayey surface formations including coarse elements of basic extrusive rocks or calcareous alluvium parent materials (Table 1). They are Cambisols (JB 1 and JB 2), Vertisols (SW 1 and TH 1) and a Clacisol (QM 1) according to the IUSS Working Group WRB (2015) (Tableau 1) and all Inceptisols according to the USDA Soil taxonomy (Soil Survey Staff, 2010) (Table 1). They are representative of the major Syrian clayey soils (Land Classification and Soil Survey of the Syrian Arab Republic, 1982) in two Syrian agro-climatic areas as defined by Khlosi et al. (2012).

Physico-chemical and hydric analyses

Undisturbed roughly parallelepiped samples 500-800 cm^3 in volume were collected in winter when the soil was near to field capacity and as a consequence near maximum swelling. The samples were stored at 4–5°C to reduce biological activity and in sealed plastic containers to avoid water loss.

Part of the samples was air-dried and manually ground in a mortar to < 2 mm material. Particle-size distribution was measured using the pipette method after pretreatment with hydrogen peroxide and sodium hexametaphosphate (Robert & Tessier 1974). The $CaCO_3$ content ($CaCO_3$, in g per g of oven-dried soil) was measured according to Dupuis (1969). Cation exchange capacity (*CEC*, in $mmol_+$ per g of oven-dried soil) and exchangeable cations (in $mmol_+$ per g of oven-dried soil) were measured using ammonium acetate buffered at pH 7.0, and organic carbon content (*OC*, in g per g of oven-dried soil) by oxidation using an excess amount of potassium bichromate in sulphuric acid controlled at

135°C (Baize, 2018). The N_2-BET external specific surface area (*SSA*, in m² per g of oven-dried soil) was measured for the < 2 mm fraction dried at 105 °C (Fripiat et al., 1971).

Centimetric clods (5 to 10 cm^3) were separated by hand from the stored decametric samples. Their water content at field capacity (W_{fc}, in g of water per g of oven dried soil) and bulk density (D_b) were measured using the kerosene method (Monnier et al., 1973). The gravimetric water content (*W*, in g of water per g of oven-dried soil) at water potentials, *h*, of –10, –33, –100, –330, –1000, –3300 and –15000 hPa was measured using a pressure membrane or pressure plate apparatus. The clods were placed on a paste made of < 2 µm particles of kaolinite to establish continuity of water between the clods and the membrane or the porous plate of the apparatus (Bruand et al., 1996).

The mineralogical composition of the < 2 µm material of the horizons was determined by X-ray diffraction (XRD) using the air dried < 2 mm material. The clay fraction was collected using the sedimentation method at 20°C after mechanical dispersion and saturated with Mg^{++} according to Robert and Tessier (1974). Oriented clay deposits were prepared on glass slides and studied using an X-ray diffractometer equipped with a Si(Li) solid detector to filter the $Cu_{k\alpha}$ radiation ($\lambda Cu_{k\alpha}$ = 1.5418 Å) of a standard European type X-ray tube (40 kV, 40 mA). The XRD patterns were collected from 2 to 24° 2θ per step of 0.05° 2θ, on successively air-dried at 20°C, glycoled, heated to 150 and then 550°C oriented clay deposits (Robert & Tessier 1974; Bruand & Prost 1986).

Criteria used to evaluate the performance of the regression equations

The performance of the regression equations established to predict the gravimetric water of the horizons was assessed using the mean error (*ME*), the standard deviation (*SD*) and the root mean square error (*RMSE*):

$$ME = \frac{1}{l}\sum_{j=1}^{l}\left(W_{p,i,j} - W_{m,i,j}\right) \qquad (1)$$

$$SD = \left\{\frac{1}{l}\sum_{j=1}^{l}\left[\left(W_{p,i,j} - W_{m,i,j}\right) - ME\right]^2\right\}^{1/2} \quad (2)$$

$$RMSE = \left\{\frac{1}{l}\sum_{j=1}^{l}\left(W_{p,i,j} - W_{m,i,j}\right)^2\right\}^{1/2} \quad (3)$$

where $W_{p,i,j}$ is the predicted gravimetric water content of the horizon at matric potential *i* for the horizon *j*, $W_{m,i,j}$ is the measured gravimetric water content of the horizon at matric potential *i* for the horizon *j*, and *l* is the number of horizons studied.

In the same way, *ME*, *SD* and *RMSE* were calculated to evaluate the performance of the equations used to predict the volumetric water content of the horizons as follows:

$$ME = \frac{1}{l}\sum_{j=1}^{l}\left(\theta_{p,i,j} - \theta_{m,i,j}\right) \quad (4)$$

$$SD = \left\{\frac{1}{l}\sum_{j=1}^{l}\left[\left(\theta_{p,i,j} - \theta_{m,i,j}\right) - ME\right]^2\right\}^{1/2} \quad (5)$$

$$RMSE = \left\{\frac{1}{l}\sum_{j=1}^{l}\left(\theta_{p,i,j} - \theta_{m,i,j}\right)^2\right\}^{1/2} \quad (6)$$

where $\theta_{p,i,j}$ is the predicted volumetric water content of the horizon at matric potential *i* for the horizon *j*, $\theta_{m,i,j}$ is the measured volumetric water content of the horizon at matric potential *i* for the horizon *j*, and *l* is the number of horizons studied.

The values of *ME* and *SD* provide information on the estimation bias and precision, respectively. The sign of ME indicates whether the prediction overestimated (positive) or underestimated (negative) the value predicted. As for *RMSE*, it varies according to both the overall prediction bias and overall prediction precision. The calculation of *ME* gives equal weight to all errors whereas *RMSE* assigns more weight to larger errors than to smaller ones. The greater the difference between *ME* and *RMSE*, the more large errors there are. Thus, the best prediction performance is recorded when ME is as close as possible to 0 and SD and RMSE are as small as possible, indicating the most unbiased and precise prediction.

144

145 Results

146 *Physico-chemical characteristics*

147 The main characteristics of the studied samples are given in Table 2. The horizons studied showed
148 very low or low $CaCO_3$ content (≤ 0.06 g g^{-1}) except for the horizons QML 1–1 and 1–2 for which the
149 $CaCO_3$ content was 0.30 and 0.31 g g^{-1}, respectively. The organic carbon content ranged from 0.002 to
150 0.008 g g^{-1}, the highest organic carbon content being recorded for the horizons A. The clay content
151 (*CC*, in g per g of oven-dried soil at 105°C) ranged from 0.43 to 0.69 g g^{-1} between the different
152 horizons studied but did not vary highly with depth in each soil (Table 2). The cation exchange
153 capacity (*CEC*, in $mmol_+$ per g of oven-dried soil at 105°C) ranged from 0.304 to 0.492 $mmol_+$ g^{-1}.
154 The external specific surface area (*SSA*, in m^2 per g of oven-dried soil at 105°C) ranged from 61 to
155 91 m^2 g^{-1}.

156

157 *Clay mineralogy*

158 The XRD patterns of the clay extracted from the horizons studied showed (Figure 1) the presence of
159 different types of clays (Robert & Tessier 1974; Bruand & Prost 1986; Moore & Reynold 1997):

160 – 1:1 clays which are kaolinite as shown by the peak at 0.72 nm which is similar at 20°C, 150°C
161 and after treatment with ethylene glycol. The absence of a peak at 0.72 nm after heating to
162 550°C confirmed the presence of kaolinite which is dehydroxylated at such a temperature;

163 – non–swelling 2:1 clays which are illite as shown by the peak at 1.12–1.02 nm at 20°C which
164 did not change after treatment with ethylene glycol. After heating at 550°C, this peak shifted
165 to 1.01 nm, indicating the closing of the magnesian interlamellar spaces;

166 – swelling 2:1 clays which are smectite as shown by the shift of the wide peak at 1.44–1.57 nm
167 at 20°C to 1.72–1.77 nm after treatment with ethylene glycol because of the swelling of the
168 interlamellar space due to intercalation of the ethylene glycol molecules. After heating at
169 550°C, all the peaks recorded for higher values than 1.01 nm disappeared, indicating the
170 closing of the magnesian interlamellar spaces due to the loss of the ethylene glycol molecules;

171 – 2:1/1 clays which are chlorites as shown by the peak at 1.42–1.47 nm similar at 20°C and after
172 treatment with ethylene glycol. The remaining peak at 1.42 nm recorded after heating at
173 550°C is indeed consistent with the presence of chlorites which are not dehydroxylated at such
174 a temperature.

175 A semi-quantitative evaluation of the content in the different types of clays identified is given in Table
176 3.

177

178 ***Water retention properties***

179 The water retention properties showed a wide variety of water content between −10 and −15000 hPa
180 matric water potential (Table 4). The smallest and highest water contents at field capacity were 0.262
181 and 0.507 g g^{-1}, respectively. This high variation in water content at field capacity was consistent with
182 the water content recorded at −10 hPa which ranged from 0.328 to 0.540 g g^{-1} and at −15000 hPa
183 which ranged from 0.207 to 0.385 g g^{-1}.

184

185 # Discussion

186 ***Physico-chemical characteristics and clay mineralogy***

187 As the soil horizons contained little organic carbon (Table 2), which is consistent with the soil organic
188 matter dynamics in semi-arid areas (Mrabet, 2011; Schellekens et al., 2013), the contribution of

organic matter to the cation exchange capacity was considered as being negligible compared with the cation exchange capacity of the clay. Indeed, if we assume that the cation exchange capacity of the organic matter of the soil studied is equal to 4 $mmol_+ g^{-1}$ of organic carbon, which is a value among the highest values recorded in the literature (Schnitzer, 1978; Tate & Theng, 1980; Stevenson, 1982), the contribution of organic matter to the *CEC* would range from 0.008 to 0.032 $mmol_+ g^{-1}$ of oven dried soil for the horizons studied. Thus, the cation exchange capacity of the clay (CEC_{cl}, in $mmol_+$ per g of oven-dried clay at 105°C) was calculated as follows:

$$CEC_{cl} = (CEC/CC) \quad (7)$$

with *CC* the clay content. Results showed that CEC_{cl} ranged from 0.707 to 0.891 $mmol_+ g^{-1}$ (Table 5), indicating that the clay fraction was mainly composed of swelling 2:1 clays (Robert & Tessier 1974; Wilson, 1999; Churchman & Velde 2019). These values of CEC_{cl} are consistent with the X-ray diffraction data (Figure 1) which show the predominance of 2/1 clay minerals with smectite content ranging from not abundant to abundant depending on the horizon (Table 3).

As the calculated surface area developed by quartz spheres with a diameter > 2 µm was < 1.1 $m^2 g^{-1}$, the contribution of both the silt and sand particles can be assumed to range from 0.2 to 0.6 $m^2 g^{-1}$ for the soil studied and therefore negligible compared to the *SSA* measured (Table 2). Thus, the external specific surface area (*SSA*) of the clay fraction was calculated (SSA_{cl}, m^2 per g of oven-dried clay at 105°C) as follows:

$$SSA_{cl} = (SSA/CC) \quad (8)$$

The results showed that SSA_{cl} ranged from 112 to 178 $m^2 g^{-1}$ (Table 5) which are high external specific surface areas for clays, indicating a very small size of the elementary clay particles in the horizons studied (Bergaya & Lagaly 2013; Churchman & Velde 2019).

Compared to the 37 clayey soils studied by Bruand and Tessier (2000), the CEC_{cl} recorded for the Syrian clayey soils studied were higher. The SSA_{cl} recorded in this study were also higher than those recorded by Bruand and Tessier (2000) except for the horizons JB 1 and JB 2 for which the SSA_{cl} were

among the highest recorded by these authors. To extend the range of both the CEC_{cl} and SSA_{cl} discussed, the relationship between CEC_{cl} and SSA_{cl} was established using both the data published by Bruand and Tessier (2000) and those recorded in this study (Figure 2). The closeness of the relationship ($R^2 = 0.78$, n = 47) is consistent with the results recorded by Bruand and Zimmer (1992) and Bigorre et al. (2000), indicating that a high proportion of CEC_{cl} variance was explained by SSA_{cl} for the soils studied and consequently by the size of the elementary clay particles (Figure 2). Thus, the cation exchange capacity of the elementary clay particles appears to be mainly related to the negative charges present on the external surfaces of these particles (Robert et al., 1991; Bergaya & Lagaly 2013). The high distance to the regression line recorded for the horizons TH 1-2, TH 1-3, QM 1-1 and QM 1-2 indicates that the interfoliar space of the elementary clay particles, which SSA_{cl} does not account for, contributes more than for the other horizons to their cation exchange capacity (Figure 2, Table 5) (Bergaya & Lagaly 2013; Churchman & Velde 2019).

Comparison of the XRD patterns with the values of CEC_{cl} and SSA_{cl} recorded showed the presence of a small amount of smectite for JB 2-1, JB 2-2 and JB 2-3 when CEC_{cl} and SSA_{cl} were among the highest values recorded (Figure 1, Tables 3 and 5). The low intensity of the peak between 1.44 and 1.57 nm at 20°C and between 1.72 and 1.77 nm after treatment with ethylene glycol (Figure 1) is in all likelihood related to the weak organization along the crystallographic plane *ab* of the elementary clay particles in the clay deposit on the glass slide because of the very small size of the elementary clay particles as indicated by SSA_{cl} (Table 5) (Tessier & Pédro 1987). The proportion of smectite in JB 2-1, JB 2-2 and JB 2-3 is therefore probably higher than that indicated by the XRD patterns (Figure 1) and reported in Table 3.

Pore volume developed by the assemblage of elementary clay particles

Assuming that water was mainly retained by the clay phase whatever the potential, as earlier shown by Bruand and Zimmer (1992), Bruand and Tessier (2000) and D'Angelo et al. (2014), we considered that for the centimetric clods at field capacity the volume of cracks and biopores was negligible

compared with the pore volume developed by the assemblage of the elementary clay particles. Thus, the specific volume of clods at the field conditions (V_{fc}) is related to the specific volume of the solid phase (V_s, in cm^3 per g of oven-dried soil) and to the specific pore volume (V_p, in cm^3 per g of oven-dried soil) as follows:

$$V_{fc} = V_s + V_p \quad (9)$$

V_p was calculated for each horizon using $V_s = 0.377$ cm^3 g^{-1} which corresponds to a particle density of 2.65 and V_{fc} which corresponds to the reciprocal of D_b measured on centimetric clods (Table 2), giving:

$$V_p = (1/D_b) - V_s \quad (10)$$

The values of V_p recorded ranged from 0.671 to 0.840 cm^3 g^{-1}. The specific pore volume of the clay ($V_{p,cl}$, in cm^3 per g of oven-dried clay) was calculated as follows:

$$V_{p,cl} = V_p/CC \quad (11)$$

The quantity $V_{p,cl}$, which can be considered as a quantitative expression of the clay fabric, ranged from 0.612 to 0.722 cm^3 g^{-1} (Table 5). This is a much smaller range of variation than that recorded for the soils studied by Bruand and Tessier (2000) ($0.337 \leq V_{p,cl} \leq 1.484$ cm^3 g^{-1}). However, it is interesting to note that although the values of CEC_{cl} recorded for the Syrian clayey horizons studied are higher than those recorded for the clayey soils studied by Bruand and Tessier (2000), 6 soils of those studied by the latter showed higher $V_{p,cl}$ than those recorded in this study, thus illustrating that $V_{p,cl}$ varies according to the clay mineralogy but also according to the hydric history of the soil (Tessier and Pédro, 1984 and 1987). In the same way, even if $V_{p,cl}$ could theoretically be assumed to be closely related to the size of the elementary clay particles, the results recorded showed the lack of a close relationship between $V_{p,cl}$ and SSA_{cl}, again because of the hydric history of the soil (Tessier and Pédro, 1984 and 1987). This is the case of the Syrian clayey soils studied with a very poor relationship between $V_{p,cl}$ and SSA_{cl} ($R^2 = 0.24$).

Water retention properties of the clay

Since the difference in water retention properties between the horizons results from the variation in both the clay content and the water retention properties of the clay, the latter were calculated by correcting the gravimetric water content of the horizon (W) for clay content (CC) at different water potentials as follows:

$$W_{cl} = W/CC \quad (12)$$

The quantity W_{cl} can be considered as the amount of water retained by the pore volume related to the clay fabric (W_{cl}, in g of water per g of oven-dried clay). Regression equations were established between W_{cl} and $V_{p,cl}$ with the data published by Bruand and Tessier (2000) and then with both the data published by these authors and those recorded in this study for Syrian clayey soils (Table 6).

Although the range of variation of CEC_{cl} and SSA_{cl} was markedly different between, on the one hand, the dataset published by Bruand and Tessier (2000) with CEC_{cl} ranging from 0.227 to 0.666 $mmol_+ g^{-1}$ and SSA_{cl} ranging from 53 to 139 $m^2 g^{-1}$ and, on the other hand, the Syrian dataset with CEC_{cl} ranging from 0.707 to 0.891 $mmol_+ g^{-1}$ and SSA_{cl} from 112 to 178 $m^2 g^{-1}$ (Table 5), the regression equations established by Bruand and Tessier (2000) (Table 6) were tested with the Syrian dataset to be able to discuss the expected improvement in the prediction quality when the regression equations are established with both datasets (Table 7). Their performance was evaluated using *ME*, *SD* and *RMSE*. Results showed that *ME* ranged from –0.065 g g^{-1} at –10 hPa water potential to 0.047 g g^{-1} at –1000 hPa water potential (mean = –0.008 g g^{-1}), *SD* from 0.042 g g^{-1} at –15000 hPa water potential to 0.069 g g^{-1} at –330 hPa water potential (mean = 0.057 g g^{-1}) and *RMSE* from 0.051 g g^{-1} at –3300 hPa water potential to 0.091 g g^{-1} at –10 hPa water potential (mean = 0.068 g g^{-1}) (Table 7).

Regression equations were established between W_{cl} and $V_{p,cl}$ using both the data recorded by Bruand and Tessier (2000) and the data recorded in this study (Table 6). They were tested successively on the two datasets by recalculating them each time without taking into account the horizon on which

289 they were tested. The number of horizons used to establish the regression equations was 46, one being
290 left out when calculating each regression equation. When tested on the dataset published by Bruand
291 and Tessier (2000), results showed that *ME* ranged from –0.011 g g^{-1} at –330 hPa and –1000 hPa
292 water potential to 0.014 g g^{-1} at –10 hPa water potential (mean = 0.001 g g^{-1}), *SD* from 0.035 g g^{-1} at –
293 3300 hPa water potential to 0.043 g g^{-1} at –10 hPa water potential (mean = 0.039 g g^{-1}) and *RMSE*
294 from 0.035 g g^{-1} at –3300 hPa water potential to 0.045 g g^{-1} at –10 hPa water potential according
295 (mean = 0.040 g g^{-1}) (Table 7). When tested on the Syrian clayey soils, results showed a lower
296 prediction performance than when tested on the French dataset, with *ME* ranging from –0.052 g g^{-1} at
297 –10 hPa water potential to 0.037 g g^{-1} at –1000 hPa water potential (mean = –0.006 g g^{-1}), *SD* from
298 0.043 at -15000 hPa water potential to 0.070 g g^{-1} at –330 hPa water potential (mean = 0.058 g g^{-1}) and
299 *RMSE* from 0.050 g g^{-1} at –3300 hPa water potential to 0.083 g g^{-1} at –10 hPa water potential (mean =
300 0.065 g g^{-1}) (Table 7). Comparison of these values with those recorded when the regression equations
301 were established with the data of Bruand and Tessier (2000) showed that the range of bias for water
302 potential ranging from –10 to –15000 hPa was reduced by 20%, with no variation in the precision
303 when the regression equations were established with both the datasets (Table 7). The overall
304 prediction quality was slightly increased, as indicated by the *RMSE* values which were reduced by
305 20% when the regression equations were established using both datasets (Table 7).

306 Thus, when clayey soils with clays developing a high CEC and a hydric history acquired in a
307 semi-arid climate are taken into account, this slightly improves the validity of using $V_{p,cl}$ to predict the
308 water retention properties of the clay of horizons belonging to soils developed under a larger range of
309 climatic environments than those already studied in the literature.

310

311 ***Water retention curve of the horizons***

312 The regression equations established between W_{cl} and $V_{p,cl}$ make it possible to predict the water
313 content at the scale of the horizon since:

$$W_i = CC \times \left[a_i + \left(b_i \times V_{p,cl}\right)\right] \quad (13)$$

with W_i, the gravimetric water content in g of water per g of oven-dried soil at the water potential i, CC, the clay content of the soil in g of clay per g of oven-dried soil, a_i and b_i, the coefficients of the regression equations at the water potential i (Table 6), and $V_{p,cl}$, the specific pore volume of the clay in cm^3 per g of oven-dried clay for the soil at field capacity. The predicted volumetric water content at water potential i (θ_i, in cm^3 of water per cm^3 of soil) can be calculated as follows:

$$\theta_i = D_b \times W_i. \quad (14)$$

Then, by using equations (7), (8) and (11):

$$\theta_i = D_b \times CC \times \left\{a_i + \left[b_i \times \left((1/D_b) - V_s\right)/CC\right]\right\} \quad (15)$$

which becomes:

$$\theta_i = D_b \times CC \times \left\{a_i + \left[b_i \times \left((1/D_b) - 0.377\right)/CC\right]\right\} \quad (16)$$

using V_s = 0.377 $cm^3\ g^{-1}$ which corresponds to a particle density of 2.65. The θ_i calculated at the different water potentials and for the different horizons were compared to the θ_i measured. Results showed *ME* ranging from –0.028 $cm^3\ cm^{-3}$ at –33 hPa water potential to 0.025 $cm^3\ cm^{-3}$ at –1000 hPa water potential (mean = –0.005 $cm^3\ cm^{-3}$), *SD* from 0.036 $cm^3\ cm^{-3}$ at -15000 hPa water potential to 0.054 $cm^3\ cm^{-3}$ at –10 and –33 hPa water potential (mean = 0.046 $cm^3\ cm^{-3}$) and *RMSE* from 0.039 $cm^3\ cm^{-3}$ at –3300 hPa water potential to 0.059 $cm^3\ cm^{-3}$ at –33 hPa water potential (mean = 0.048 $cm^3\ cm^{-3}$) (Table 8).

These results can be compared with those recorded earlier with soils located in semi-arid areas. Tombul et al. (2004) applied early pedotransfer functions established using multiple linear regression to 126 horizons originating from soils developed in a semi-arid area in Turkey. They compared the measured and predicted volumetric water contents at –330 and –15000 hPa and recorded a mean *RMSE* of 0.072 and 0.030 $cm^3\ cm^{-3}$, respectively. Mosaddeghi and Mahboubi (2011) studied the water

retention properties of 63 soils located in a semi-arid area of western Iran. They developed pedotransfer functions using multiple linear regression and the comparison of the measured and predicted volumetric water content at 11 water potentials between –10 and –15000 hPa led to *RMSE* ranging from 0.034 to 0.044 $cm^3\ cm^{-3}$ for the 63 topsoils and from 0.034 to 0.047 $cm^3\ cm^{-3}$ for the subsoils. More recently, Dharumarajan et al. (2019) established pedotransfer functions using also multiple linear regression for soils developed in a semi-arid area of India. They studied 740 horizons originating from 149 soils with varying textures. The *RMSE* recorded when they compared the measured and predicted volumetric water content at –330 and –15000 hPa was 0.046 and 0.032 $cm^3\ cm^{-3}$, respectively.

Using multiple linear regression, artificial neural networks and support vector machines, Khlosi et al. (2016) discussed the performance of pedotransfer functions established with Syrian soils which were mainly loam, clay loam and clay soils. They applied their pedotransfer functions to 18 horizons originating from Syrian soils and recorded values of *RMSE* higher than those recorded in this study with RMSE ranging from 0.065 to 0.089 $cm^3\ cm^{-3}$ (mean = 0.080 $cm^3\ cm^{-3}$) with multiple linear regressions, from 0.055 to 0.075 $cm^3\ cm^{-3}$ (mean = 0.067 $cm^3\ cm^{-3}$) with artificial neural networks and from 0.048 to 0.064 $cm^3\ cm^{-3}$ (mean = 0.058 $cm^3\ cm^{-3}$) with support vector machines.

As the size of the datasets used in these different studies was highly variable and larger than in our study, the comparison with our results and between the different studies remains limited to the observation that the RMSE values are of the same order of magnitude. In our study, we used only two soil characteristics, the clay content and the bulk density when the soil was close to field capacity, when the above studies have used much more soil characteristics. Our results indicate for soils of semi-arid areas the interest of developing pedotransfer functions which take variables closely related to the water retention mechanisms in soils more into account. The values of θ calculated with the proposed equations at the different water potentials can be used to fit a model of water retention curve which is usually required to predict plant-available water and more generally, to run plant-soil-water models. Future work will aim at enlarging both the range of textures and of climatic conditions under

which the clayey soils developed, with the aim of studying the way in which their water retention properties are related to the hydric history.

Conclusion

Our objective was to analyze the water retention properties of clayey soils developed in semi-arid areas of Syria and to discuss how these properties could be explained by the characteristics of the clay. Results showed that the clay of the soils studied has both a higher cation exchange capacity and a higher external specific surface area than those recorded for clayey soils studied in temperate areas and used as a reference in this study. The cation exchange capacity and external specific surface area values recorded are consistent with the clay mineralogy, as shown by the X-ray diffraction data which revealed the presence in most horizons of a high proportion of smectite and secondarily a varying proportion of illite and chlorite, while kaolinite was present but not abundant. Results also showed that the amount of water retained by the clay at water potentials ranging from –10 to –15000 hPa was closely related to the specific pore volume developed by the elementary clay particles at field capacity. Thus, regression equations established by using both the data earlier published and those recorded in this study were proposed to predict the water retention properties of clayey soils over a larger range of clay mineralogies and climatic environments than previously reported in the literature. The specific pore volume as well as the clay content were found to be the most important predictors of water retention properties, the former corresponding to the pore volume developed by the elementary clay particles which varies according to the clay mineralogy and hydric history of the soil. Finally, from a more applied point of view, our results showed the significance of the bulk density measured in conditions close to the field capacity to predict the water retention properties of clayey soils. It should be more systematically measured during soil studies.

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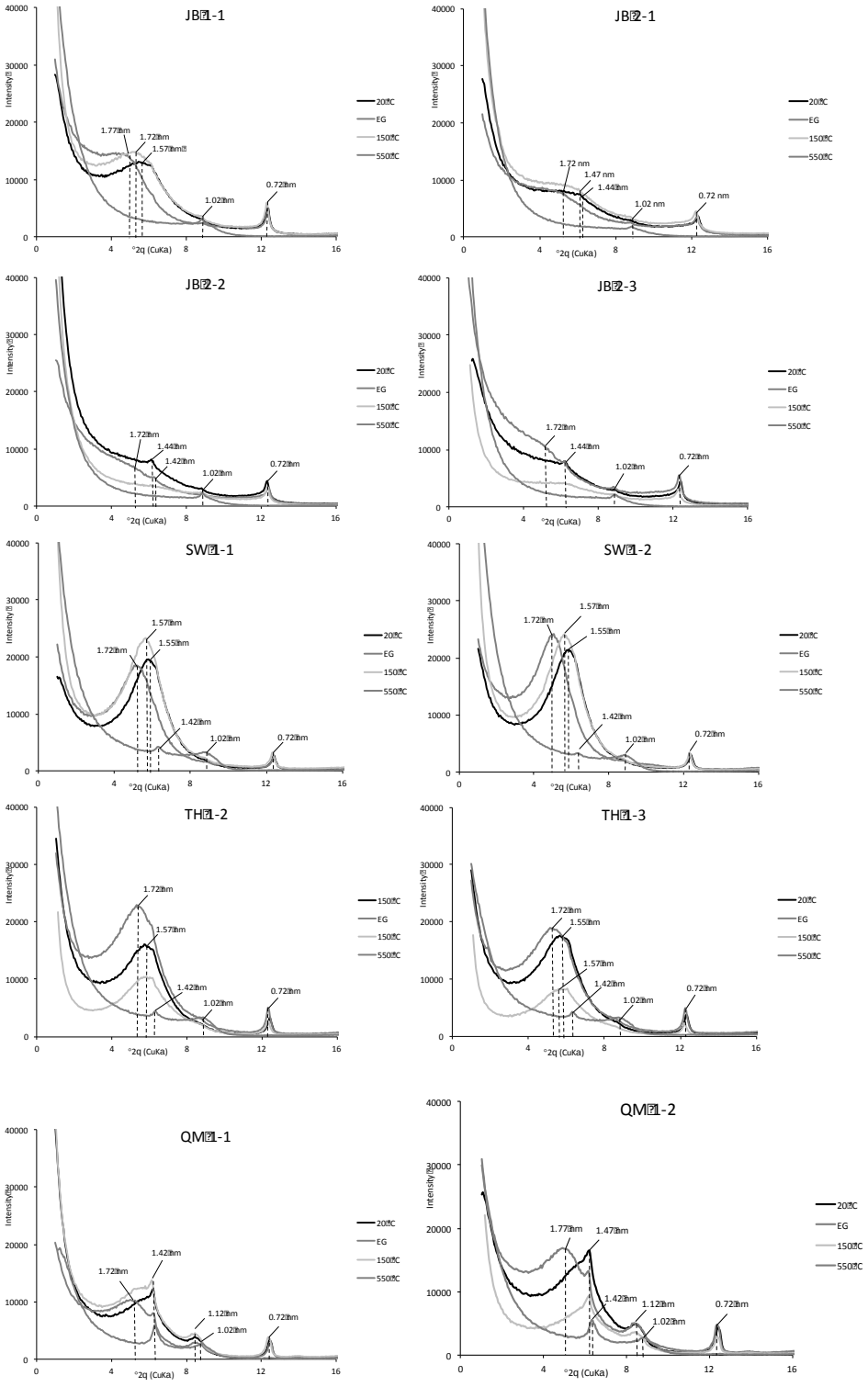

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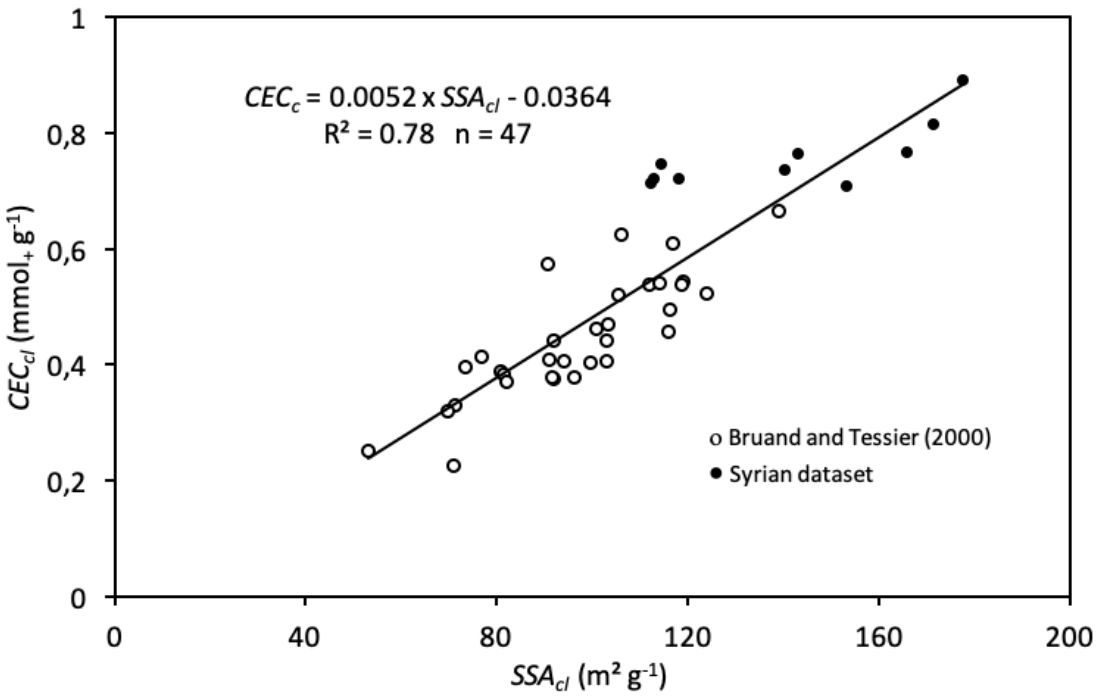

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604 **Table 1**. Main characteristics of the soils studied.

Soil location	Coordinates UTM	Soil type Soil Survey Staff (2010) / IUSS Working Group WRB (2015)	Parent material	Land use	Agro-climatic zone
Jabbah (JB 1)	33.1623N – 35.9368E	Typic Haploxerept / Hypereutric Cambisol	Clayey surface formations including coarse elements of basic extrusive rocks	Meadow	1
Jabbah (JB 2)	33.1520N – 35.9243E	Typic Haploxerept / Hypereutric Cambisol		Meadow	1
Al-Suwayda (SW 1)	32.7118N – 36.5494E	Vertic Chromoxerept / Chromic Vertisol		Annual crops	2
Al-Tha'Ala (TH 1)	32.7115N – 36.4860E	Vertic Xerochept / Chromic Vertisol		Olive trees	2
Al-Qamishli (QM 1)	41.0324N – 41.1303E	Calcic Xerocrept / Vertic Calcisol	Calcareous alluvium materials	Annual crops	1

605 Agro-climatic zones according to Khlosi et al. (2012): zone 1 is characterized by a mean annual precipitation >300 mm in 2 out of 3 seasons and shrubland, degraded forest, rock outcrops and
606 permanent crops; zone 2 is characterized by a mean annual precipitation of 250-300 mm 2 out of 3 seasons, permanent crops and rainfed field crops with irrigated crops.

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611 **Table 2**. Main characteristics of the horizons studied.

Soil Sample	Horizon	Depth cm	Texture	D_b	Particle size distribution g.g^{-1}			$CaCO_3$ g.g^{-1}	*OC* g.g^{-1}	*CEC* mmol$_+$.g^{-1}	Exchangeable cations mmol$_+$.g^{-1}				*SSA* m².g^{-1}
					Clay <2µm	Silt 2-50 µm	Sand 50-2000µm				Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	
JB 1-1	A	5-25	F	1.48	0.43	0.34	0.23	≤0.01	0.008	0.304	0.180	0.086	0.019	0.010	65.9
JB 2-1	A	5-25	F	1.49	0.45	0.29	0.26	≤0.01	0.008	0.345	0.202	0.099	0.020	0.010	74.7
JB 2-2	B	30-60	F	1.44	0.46	0.30	0.24	≤0.01	0.004	0.375	0.208	0.113	0.016	0.008	78.9
JB 2-3	B	60-80	F	1.41	0.46	0.31	0.23	0.02	0.002	0.410	0.209	0.116	0.010	0.007	81.7
SW 1-1	A	0-25	F	1.26	0.58	0.22	0.20	0.04	0.004	0.442	0.306	0.097	0.008	0.009	83.0
SW 1-2	B	30-70	VF	1.28	0.65	0.16	0.19	0.05	0.002	0.478	0.333	0.093	0.010	0.007	91.3
TH 1-2	B	25-50	VF	1.28	0.66	0.15	0.19	0.06	0.003	0.475	0.294	0.119	0.016	0.011	74.6
TH 1-3	B	50-75	VF	1.25	0.69	0.11	0.20	0.06	0.002	0.492	0.317	0.082	0.024	0.008	77.6
QM 1-1	A	0-25	F	1.32	0.53	0.25	0.22	0.30	0.006	0.395	0.290	0.082	0.010	0.005	60.8
QM 1-2	B	25-50	F	1.34	0.57	0.24	0.19	0.31	0.004	0.410	0.320	0.089	0.006	0.003	67.4
Mean	–	–	–	1.36	0.55	0.24	0.21	0.087	0.004	0.413	0.266	0.098	0.014	0.008	75.6
SD	–	–	–	0.09	0.09	0.08	0.03	0.111	0.002	0.058	0.059	0.014	0.006	0.002	8.6
Min	–	–	–	1.25	0.43	0.11	0.19	0.01	0.002	0.305	0.180	0.082	0.006	0.003	60.8
Max	–	–	–	1.49	0.69	0.34	0.26	0.31	0.008	0.492	0.333	0.119	0.024	0.011	91.3

612 Texture according to the FAO triangle (FAO, 1990), F: Fine, VF: Very Fine; D_b, bulk density; $CaCO_3$, calcium carbonate content; *OC*: organic carbon content; *CEC*, cation exchange capacity; *SD*,
613 standard deviation.
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617 **Table 3**. Semi-quantitative evaluation of clay minerals identified by DRX.

Soil Sample	Clay minerals			
	Kaolinite	Illite	Smectite	Chlorite
JB 1-1	+	+	++	–
JB 2-1	+	+	+	–
JB 2-2	+	+	+	–
JB 2-3	+	+	+	–
SW 1-1	+	–	+++	+
SW 1-2	+	–	+++	+
TH 1-2	+	–	+++	+
TH 1-3	+	–	+++	+
QM 1-1	+	++	++	++
QM 1-2	+	++	++	++

618 +++ abundant, ++ moderately abundant, + not abundant, – not identified.

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622 **Table 4**. Water content at field conditions (W_{fc}, g g^{-1}) and at different water potentials (W_h, g g^{-1}).

Soil sample	W_{fc}	Water retained at a water potential of hPa (g g^{-1})						
		W_{-10}	W_{-33}	W_{-100}	W_{-330}	W_{-1000}	W_{-3300}	W_{-15000}
JB 1-1	0.318	0.360	0.343	0.303	0.272	0.261	0.242	0.222
JB 2-1	0.262	0.331	0.301	0.284	0.254	0.241	0.236	0.207
JB 2-2	0.283	0.328	0.320	0.296	0.261	0.248	0.244	0.224
JB 2-3	0.292	0.342	0.330	0.317	0.265	0.251	0.245	0.224
SW 1-1	0.371	0.445	0.439	0.433	0.352	0.320	0.316	0.279
SW 1-2	0.375	0.447	0.424	0.408	0.340	0.338	0.322	0.279
TH 1-2	0.472	0.534	0.508	0.468	0.431	0.311	0.302	0.270
TH 1-3	0.507	0.540	0.532	0.483	0.451	0.423	0.414	0.385
QM 1-1	0.342	0.402	0.397	0.342	0.299	0.287	0.265	0.249
QM 1-2	0.344	0.382	0.357	0.341	0.302	0.290	0.264	0.255
Mean	0.357	0.411	0.395	0.368	0.323	0.297	0.285	0.259
SD	0.075	0.075	0.076	0.070	0.067	0.052	0.053	0.048
Min	0.262	0.328	0.301	0.284	0.254	0.241	0.236	0.207
Max	0.507	0.540	0.532	0.483	0.451	0.423	0.414	0.385

623 *SD*, standard deviation.
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628 **Table 5**. Characteristics calculated for the clay of the
629 Syrian soils studied.

Soil Sample	CEC_{cl} $mmol_+.g^{-1}$	SSA_{cl} $m^2.g^{-1}$	$V_{p,\,cl}$ $cm^3.g^{-1}$
JB 1-1	0.707	153	0.695
JB 2-1	0.767	166	0.654
JB 2-2	0.815	172	0.690
JB 2-3	0.891	178	0.722
SW 1-1	0.762	143	0.718
SW 1-2	0.735	141	0.622
TH 1-2	0.720	113	0.613
TH 1-3	0.712	112	0.612
QM 1-1	0.745	115	0.718
QM 1-2	0.719	118	0.648
Mean	0.757	141	0.669
SD	0.054	24	0.042
Min	0.707	112	0.612
Max	0.891	178	0.722

630 CEC_{cl}, cation exchange capacity of the clay; SSA_{cl}, specific surface
631 area of the clay; $V_{p,cl}$, specific pore volume of the clay
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Table 6. Regression equations between the water content of clay (W_{cl}) at different water potentials and the clay fabric ($V_{p,\,cl}$) calculated with the data published in tables 1, 2 and 3 by Bruand and Tessier (2000).

Water potential hPa	Regression equations calculated:					
	with the data published by Bruand and Tessier (2000) (n=37)			with both the data published by Bruand and Tessier (2000) and those recorded in this study (n=10)		
		R^2	*N*		R^2	*N*
–10	$W_{cl} = -0.0184 + 1.0516\ V_{p,\,cl}$	0.96	37	$W_{cl} = -0.0107 + 1.0615\ V_{p,\,cl}$	0.92	47
–33	$W_{cl} = -0.0150 + 1.0327\ V_{p,\,cl}$	0.96	37	$W_{cl} = -0.0087 + 1.0378\ V_{p,\,cl}$	0.93	47
–100	$W_{cl} = -0.0310 + 1.026\ V_{p,\,cl}$	0.96	37	$W_{cl} = -0.0244 + 1.0201\ V_{p,\,cl}$	0.94	47
–330	$W_{cl} = -0.0231 + 0.9779\ V_{p,\,cl}$	0.96	37	$W_{cl} = -0.0135 + 0.9474\ V_{p,\,cl}$	0.92	47
–1000	$W_{cl} = -0.0027 + 0.8865\ V_{p,\,cl}$	0.96	37	$W_{cl} = +0.0030 + 0.8613\ V_{p,\,cl}$	0.92	47
–3300	$W_{cl} = +0.0484 + 0.7387\ V_{p,\,cl}$	0.95	37	$W_{cl} = +0.0531 + 0.7239\ V_{p,\,cl}$	0.91	47
–15000	$W_{cl} = +0.1462 + 0.4269\ V_{p,\,cl}$	0.84	37	$W_{cl} = +0.1479 + 0.4388\ V_{p,\,cl}$	0.77	47

Table 7. Mean error of prediction (*ME*), standard deviation (*SD*) and root mean square error (*RMSE*) recorded with the regression equations established between the gravimetric water content of clay (W_{cl}, in g g^{-1} of oven dried clay) at different water potentials and the pore volume developed by the elementary clay particles ($V_{p,\,cl}$, in cm^3 g^{-1} of oven dried clay) at field capacity.

Water potential hPa	*ME*, *SD* and *RSME* recorded with the regression equations established:								
	with the data published by Bruand and Tessier (2000) when applied to: (n=37)			with both the data published by Bruand and Tessier (2000) and those recorded in this study when applied to: (n=46)					
	the horizons of this study (n=10)			the horizons studied by Bruand and Tessier (2000) (n=37)			the horizons of this study (n=10)		
	ME	*SD*	*RMSE*	*ME*	*SD*	*RMSE*	*ME*	*SD*	*RMSE*
–10	–0.065	0.067	0.091	+0.014	0.043	0.045	–0.052	0.068	0.083
–33	–0.044	0.066	0.077	+0.010	0.040	0.040	–0.035	0.067	0.073
–100	–0.014	0.058	0.056	+0.002	0.040	0.039	–0.011	0.059	0.057
–330	+0.044	0.069	0.079	–0.011	0.041	0.042	+0.034	0.070	0.075
–1000	+0.047	0.050	0.067	–0.011	0.037	0.038	+0.037	0.051	0.061
–3300	+0.021	0.049	0.051	–0.005	0.035	0.035	+0.017	0.050	0.050
–15000	–0.043	0.042	0.058	+0.011	0.040	0.041	–0.034	0.043	0.053
Mean	–0.008	0.057	0.068	0.001	0.039	0.040	–0.006	0.058	0.065
Min	–0.065	0.042	0.051	–0.011	0.035	0.035	–0.052	0.043	0.050
Max	+0.047	0.069	0.091	+0.014	0.043	0.045	+0.037	0.070	0.083

Table 8. Mean error of prediction (*ME*), standard deviation (*SD*) and root mean square error (*RMSE*) recorded with the regression equations established between the volumetric water content of clay (θ_h, in $cm^3\ cm^{-3}$) at different water potentials *h* and both the clay content and the reciprocal of bulk density measured in conditions close to field capacity with both the data published by Bruand and Tessier (2000) and those recorded in this study when applied to the horizons of this study.

Water potential (hPa)	n=10		
	ME (cm^3/cm^3)	*SD* (cm^3/cm^3)	*RMSE* (cm^3/cm^3)
–10	–0.024	0.054	0.054
–33	–0.028	0.054	0.059
–100	–0.011	0.046	0.045
–330	+0.021	0.053	0.054
–1000	+0.025	0.039	0.044
–3300	+0.010	0.039	0.039
–15000	–0.025	0.036	0.042
Mean	–0.005	0.046	0.048
Min	–0.028	0.036	0.039
Max	+0.025	0.054	0.059