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Published Version:
Tlili, A., Dridi, I., De Feudis, M., Vittori Antisari, L., Jedidi, N. (2025). Boron characterization and distribution in particle-size fractions and humic substances in forest and agricultural Tunisian soils. EURO-MEDITERRANEAN JOURNAL FOR ENVIRONMENTAL INTEGRATION, 10, 1-1767 [10.1007/s41207-024-00604-1].

Availability:
This version is available at: https://hdl.handle.net/11585/996634 since: 2024-11-15

Published:
DOI: http://doi.org/10.1007/s41207-024-00604-1

Boron characterisation and distribution in particle-size fractions and humic substances in forest and agricultural Tunisian soils

Ahlem Tlili [1,2*], Imene Dridi [2], Mauro De Feudis[3*], Livia Vittori Antisari [3,4], Naceur Jedidi [1]

[1] Water Research and Technology Center, 8020 Soliman, Tunisia;

[2] Department of Geology, Faculty of Sciences of Tunis, University of Tunis El Manar, 2092, El Manar II, Tunis, Tunisia;

[3] Department of Agricultural and Food Sciences, Alma Mater Studiorum-University of Bologna, Via Fanin 40, 40127 Bologna, Italy;

[4] Centro Sperimentale per lo Studio e l'Analisi del Suolo, Alma Mater Studiorum-University of Bologna, Via Fanin 40, 40127 Bologna, Italy

* Corresponding author: Ahlem TLILI
Ahlem_tlili@outlook.com

ABSTRACT

Background: Understanding boron (B) distribution within soil components is fundamental for assessing B dynamics and availability to plants.

Aims: This research aimed to quantify B fractions and investigate the distribution of available B in particle-size fractions and total B in humic substances at different depths of soils located in northwest Tunisia.

Methods: Four agricultural soils (Luvisol, Vertisol, Cambisol, Fluvisol) and two forest soils (2 Luvisol) were selected. We analysed the main physicochemical soil properties and quantified B fractions (readily soluble "Rs-B", oxide bound "Ox-B", organically bound "Org-B", Residual "Res-B" and total B). Additionally, soils underwent particle size (sand, silt, and clay) and humic fractionation (fulvic acid "FA", humic acid "HA" and humin "H") to quantify B in each fraction.

Results: The soil available B amounts increased with depth in forest and decreased with depth in agricultural lands. The total B amount recorded in soils derived from sedimentary rocks was higher than those derived from igneous rocks. The relative proportion of B in various fractions followed the order Res-B>Org-B>Ox-B>Spa-B>Rs-B. The particle-size fractionation showed that the silt fractions recorded a higher amount of available B compared to sand and clay fractions. Moreover, the B distribution in humic substances showed that HA contains more B than FA.

Conclusions: Soil B distribution depended on soil parent material, land use, and soil characteristics. Forest soils showed greater available B content than in agricultural soils. The particle-size fractionation showed that silt contained more B than clay fraction. The humic substances extraction revealed that more B was recorded in HA than FA.

Keywords: available boron, boron fractions calcareous soils, clay, humic acid

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1. INTRODUCTION

Boron (B) is an essential micronutrient required for normal plant growth and development. It is the only element present in soil solution as a non-ionized species (Kaundal et al., 2014; Nath et al., 2018a). It is a very critical element because the ranges between deficiency and toxicity are tight (Saleem et al., 2011; Barman et al., 2017). The B amount in soils varied widely with soil types and environment. B deficiency is widespread around the globe and is commonly observed in coarse-textured acid of high rainfall areas, calcareous soils (more than 15% $CaCO_3$) with high pH, (above 7), and also in soils having low organic matter content (Prasad et al., 2014; Barman et al., 2017; Kumari et al., 2017; Nath et al., 2018a). B deficiency occurs in highly leached acid soils, fine textured calcareous and alkaline soils where calcium carbonate act as a sink for B (Laik et al., 2021). On the other hand, it has been indicated that B toxicity occurs in semi-arid and arid areas and saline soils with drainage problems due to the irrigation water high in B (Ranjbar and Jalali, 2013; Padbhushan and Kumar, 2017). Plenty of literature reported that the mobility, transport, and partitioning of B are affected by several soil factors, including parent material, pH, organic matter content, soil texture, clay minerals types, sesquioxides (Fe and Al oxides) and carbonates contents (Prasad et al., 2014; Nath et al., 2018b; Gürel et al., 2019; Padbhushan et al., 2019). Consequently, B needs to be managed accurately through the understanding of the mobility and retention of B in soils and the processes that control their availability (Kaundal et al., 2014).

B is found in soil solution, organic matter (OM), and adsorbed to minerals and humic particles and insoluble form (Padbhushan and Kumar, 2017; Laik et al., 2021). B in soil solution is easily available for plant uptake and is determined by the hot water method (Berger and Truog, 1939). The critical deficiency level of available B in soils is considered to be at 0.5 mg kg^{-1} (Katyal and Randhawa, 1983; Rattan et al., 2008). In addition, soil B is found in five different fractions, viz. the readily soluble (Rs-B), specifically adsorbed (Spa-B), oxide bound (Ox-B), organically bound (Org-B), and residual (Res-B) (Hou et al., 1994; Hou et al., 1996). The relative amount of these fractions depends on soil properties. Fractionation of B in soils provided a better understanding of B chemistry (Datta et al., 2002). Several studies (Jin et al., 1987; Padbhushan and Kumar, 2015; Barman et al., 2017; Gürel et al., 2019; Kasture et al., 2020) reported that residual B fraction represents the major percentage of total soil B but it was not related to the available B (plant uptake B). Moreover, Raza et al. (2002) found that the residual B fraction exists in the soil mineral particles. Indeed, soil mineral particles (sand, silt and clay) play an important role in soil structure, nutrient availability, and water retention. Therefore, the assessment of B distribution in soil mineral particles (sand, silt and clay) is very important to understand B mobility and retention in the soils. It is known that B availability strongly depends on soil texture. Leaching losses of B from sandy soils are very high promoting B deficiency, conversely, B deficiency in silt and clay soils is prevented (Saleem et al., 2011). Therefore, fine-textured soils often contain more available B than coarse-textured soils (Saleem et al., 2011; Prasad et al., 2014; Dridi et al., 2018; Nath et al., 2018b). Although soil texture is one of the major soil factors influencing B content, comes just from correlation analysis carried out between soil mineral particles (sand, silt, and clay fractions) and available B. However, few studies (Maurice, 1971; Tlili et al., 2019) investigated B distribution in soil mineral particles (sand, silt, and clay) extracted through particle-size fractionation.

In addition, most of the studies focused on the status of inorganic B interactions (Prasad et al., 2014; Nath et al., 2018b; Gürel et al., 2019; Padbhushan et al., 2019), while few studies have considered investigating B in humus forms (humic substances) in soils (Pennisi et al., 2010; Kot et al., 2012; Zalba et al., 2017). Indeed, humic substances (fulvic acid, humic acid, and humin) are considered the main components of soil organic matter, affecting soil physical, chemical, and biological properties. Such substances improve soil moisture and structure and enhance soil fertility by releasing nutrients from soil mineral particles (Matuszak-Slamani et al., 2017; Gayathri et al., 2020). Therefore, humic substances can potentially act as a significant reservoir of B. Recent studies experimented effects of the humic treatments on soil B content (Karaman et al., 2013; Kaptan et al., 2015; Karaman et al., 2017; Tabelin et al., 2018; Arrobas et al., 2022). However, few studies (Pennisi et al., 2010; Zalba et al., 2017) have investigated B in the extracted humic substances to determine the major B sink in humic substances. Pennisi et al. (2010), in an investigation conducted in the soil epipedon in San Vitale pinewood (Ravenna, Italy) reported that the fulvic acids (FA) contained more B with respect to the humic acids (HA). However, Zalba et al. (2017) stated that the HA is more enriched in B than the FA. Currently, more information on B status in humic substances is needed.

Currently, no such information is available on the status of B in Tunisia. Thus, it is important to throw light on the distribution of B and the factors controlling its availability in Tunisian soils which are scanty. For this reason, an attempt is made to appraise the B status in different soil types located in northwest Tunisia. Specifically, the present work aimed to (1) assesses the depth-wise distribution of available B (2) quantify the different boron fractions in soil (3) investigate B distribution in particle-size fractions (sand, silt, and clay) (4) study B distribution in humic substances (fulvic acids, humic acids, and humin).

2. MATERIALS AND METHODS

2.1. Study sites

Six soil profiles developed under contrasted pedological and bioclimatic conditions were dug northwest of Tunisia. Overall, we have selected four agricultural soils developed under calcareous parent materials and two forest soils developed under sandstone and rhyolitic parent material (Figure 1 and Table 1). In each sampling area, one soil profile was dug till parent material, and the paedogenic horizons were identified (Table A1 of the Supplementary materials) and classified according to the World Reference Base for Soil Resources system (IUSS Working Group, 2014).

2.1. Physicochemical soil analysis

Soil samples were taken from each horizon of the six studied soil profiles, air-dried, and sieved through a 2 mm stainless sieve. The soil particle size distribution was determined by the Robinson pipette method (Robinson, 1922). The soil pH and the electrical conductivity (EC) were measured in a suspension of 1:2.5 and 1:5 soil: water ratio, respectively, using the pH meter model HI-2002 Edge. The total calcium carbonate ($CaCO_3$) content was measured by the volumetric method (Bernard calcimeter) (Nelson, 1982). The organic carbon (OC) and total nitrogen (TN) contents were determined by the modified Walkley-Black method (Nelson and Sommers, 1982) and the Kjeldahl method (Bremner, 1996), respectively. The available phosphorus (P_2O_5) was determined according to Olsen and Sommers (1982). The exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) were extracted with ammonium acetate at pH 7 and measured by atomic absorption spectrometry (AAS, Perkin Elmer AAnalyst 400) (Sumner and Miller, 1996). The available B was estimated using the hot water method (Berger and Truog, 1939). The total amount of Ca, K, Mg, P, S and B were extracted by aqua regia in a microwave digestion system (Milestone Ethos 900) at 280 °C and 55 bars (Vittori Antisari et al., 2014; De Feudis et al., 2021) and their amount were measured using an inductively coupled plasma optical emission spectrometer (ICP–OES, Ametek, Spectro Arcos, Germany).

2.2. Boron fractionation

The soil B fractions were obtained using the sequential extraction method proposed by Hou et al. (1994; 1996). Briefly, the readily soluble B fraction (Rs-B) was obtained by 0.01 M calcium chloride ($CaCl_2$) and shaken for 16 hours. After centrifuging at 10,000 rpm for 30 min the supernatant solution was filtered through Whatman no 42-filter paper. The specifically adsorbed fraction (Spa-B) was extracted by 0.05 M monopotassium phosphate (KH_2PO_4) and shaken for 1 hour. After centrifugation, B was measured in the clear supernatant as described in the previous step. The oxide bound fraction (Ox-B) was determined by 0.2 M acidic NH_4-oxalate and shaken for 4 hours followed by filtration through Whatman no. 42. The organically bound fraction (Org-B) was extracted using 0.02 M HNO_3 and 30% H_2O_2. Finally, the residual fraction (Res-B) was calculated as the difference between total B and the first four fractions). B amount was quantified by ICP–OES.

2.3. Particle-size fractionation

Soil samples were separated according to the soil mineral fraction, namely sand fraction (2000-50 µm), silt fraction (2–50 µm), and clay fraction (<2 µm) as described in Tlili et al. (2019). Then each fraction was dried in an oven at 40°C to reach a constant weight. The available B amount of sand, silt, and clay fractions were extracted by hot-water methods (Berger and Truog, 1939) and analysed by ICP–OES.

2.4. Humic substances extraction

The humic substances namely fulvic acid (FA), humic acid (HA) and humin (H) were extracted according to Agnelli et al. (2014). Briefly, 100 mL of 0.1 M NaOH + 0.1 M Na_4P2O_7 solution was added to 10 g of soil, shaken for 24 h at 25 ◦C and centrifuged. The NaOH + Na_4P2O_7 extract was filtered through a 0.45 µm polycarbonate filter, while the remaining precipitate, containing the humin was washed using deionized water to remove the excess of Na until the pH of the rinsed solution was ≤ 7. After that, the humin– was air–dried at 40 °C. The 0.45 µm filtered NaOH + Na_4P2O_7 extract was acidified to about pH 1.5 with 6 M HCl and allowed to settle overnight to separate FA and HA and centrifuged. To remove the excess of Na from the obtained fractions, the supernatant (FA) was dialyzed through 1000 Da cut–off membranes (Spectra/Por® Dialysis membrane) against distilled water, while the residual (HA) was washed with distilled water. Both purified fractions were freeze-dried (Audette et al., 2021). The obtained fractions were weighted and microwave digested with HNO_3 (65% v/v)–H_2O_2 (30% v/v) for FA and HA and with aqua regia for H. The total B amount within the fractions was measured by ICP–OES.

2.5. Statistical analyses

Data are presented with a mean (average of replicates for each analysis) ± standard deviation. To assess the differences between the calcareous and non-calcareous soils, we performed a Mann-Whitney U test on the data. This non-parametric test was used due to the non-normal distribution of the data and the unequal variances between the two groups. A significance level of alpha = 0.05 was used to determine statistical significance. Furthermore, the data were subjected to correlation analysis to study the relationship between the soil properties and boron (available and total amount) and to investigate the interrelationships between B fractions, total boron and available boron. Origin Pro (ver. 8.5; OriginLab Corporation, Northampton, MA, USA) was used to create the correlation matrix. All statistical analyses were performed using the SPSS v.25.0 software program (IBM, Chicago, IL, USA).

3. RESULTS

3.1. Total and available B dynamics

The physicochemical analyses of the studied soils are presented in Table 2. Available B and total B amounts recorded in the studied soils and its depth distribution are presented in Table 3. The total B amount varied from 58.78 to 104.65 mg kg^{-1} with an average of 82.96 mg kg^{-1} in the Luvisol-1, Vertisol, Cambisol and Fluvisol (calcareous soils) and from 54.87 to 92.28 mg kg^{-1} with an average of 72.21 mg kg^{-1} in the Luvisol-2 and Luvisol-3 (non-calcareous soils). A Mann-Whitney U test indicated, on average, that total B of the calcareous soils was significantly higher than those of the non-calcareous soils. The content of available B varied from 0.21 to 1.28 mg kg^{-1} with an average of 0.75 mg kg^{-1} in the Luvisol-1, Vertisol, Cambisol and Fluvisol and from 0.82 to 2.14 mg kg^{-1} with an average of 1.44 mg kg^{-1} in the Luvisol-2 and Luvisol-3. The Available B increased with the increase of depth in the Luvisol-2. It raised from 1.19 mg kg^{-1} in the surface horizon to 2.03 mg kg^{-1} in the deep horizon. Indeed, a slight impoverishment was recorded in the sub-horizon. However, the available B content investigated in the Luvisol-1 dropped from 0.50 mg kg^{-1} in the surface horizon to 0.21 mg kg^{-1} in the deep horizon. A slight enrichment was recorded in the sub-horizon (0.61 mg kg^{-1}). Likewise, the available B amount recorded in the Vertisol dropped from 0.62 mg kg^{-1} in the surface horizon to 0.44 mg kg^{-1} in the sub-horizon and increased in the deep horizon to reach 0.68 mg kg^{-1}. Nevertheless, in the Cambisol, available B increased from 1.04 mg kg^{-1} in the surface horizon to 1.28 mg kg^{-1} in the sub-horizon then it decreases to 0.28 mg kg^{-1} in the deep horizon. The available B amount in the Luvisol-3 increased from 1.15 mg kg^{-1} to 1.40 mg kg^{-1} respectively from the surface to the deep horizon. However, an enrichment was recorded in the sub-horizon (2.14 mg kg^{-1}). Despite a decreasing trend recorded in the Fluvisol. The available B drop from 1.20 mg kg^{-1} to 0.43, respectively from surface horizon to sub-horizon, then increase to reach 1.16 mg kg^{-1}. The Mann-Whitney U test indicated, on average, that available B of the non-calcareous soils was significantly higher than those of the calcareous soils.

3.2. B fractions distribution

B amounts measured in different B fractions are expressed as % of the total B content, as presented in Table 3. In the Luvisol-1, Vertisol, Cambisol and Fluvisol, the proportion of Rs-B (0.45-1.45 %; mean 0.80%) was lower than the percentage of Spa-B (0.16-3.93%; mean 0.99%), Ox-B (0.06-14.09%; mean 3.29%), Org-B (1.37-21.22%; mean 5.31%) and Res-B (70.22-97.53%; mean 89.50%). As for the Luvisol-2 and Luvisol-3, the proportion of Rs-B (0.41-1.77 %; mean 1.21%) was lower than the percentages of Spa-B (0.59-2.09 %; mean 1.25%), Ox-B (5.78-37.77%; mean 23.37%), Org-B (6.56-35.79%; mean 23.25%) and Res-B (26.67-78.16%; mean 50.74%). In general, B amounts in the extracted fractions in all the studied soils increased in the following order: Rs-B < Spa-B < Ox-B < Org-B < Res-B. The Mann-Whitney U test indicated, on average, that Rs-B, Spa-B, Org-B and Ox-B of the non-calcareous soils were significantly higher than those of the calcareous soils. However, it revealed that the Res-B of the non-calcareous soils was significantly lower than that of the calcareous soils.

3.3. Available B distribution in particle-size fractions

The data on available B distribution in different particle-size fractions, namely sand, silt, and clay fractions are shown in Figure 2. The results were expressed as % of the respective total available B content extracted from all the particle-size fractions in each horizon. The available B recorded in sands fractions varied from 32 to 52% for the Luvisol-1, Vertisol, Cambisol and Fluvisol and from 7 to 29% for the Luvisol-2 and Luvisol-3. For silts fractions, the available B ranged from 30 to 61% for the Luvisol-1, Vertisol, Cambisol and Fluvisol and from 40 to 72% for the Luvisol-2 and Luvisol-3. The available B investigated in clay fractions varied from 0.3 to 21% for the Luvisol-1, Vertisol, Cambisol and Fluvisol and from 5 to 53% for the Luvisol-2 and Luvisol-3. In addition, it appears that the silts and clays of the Luvisol-2 and Luvisol-3 have significantly higher available B contents than those of the Luvisol-1, Vertisol, Cambisol and Fluvisol. Overall, the silt fraction contained the highest percentage of available B, the sand a lesser amount, and the clay the least amount.

3.4. Total B distribution in humic substances

The data on B distribution within FA, HA and H are presented in Figure 3. The results were expressed as % of the respective total B content extracted from the humic substances in each horizon. In the Luvisol-1, Vertisol, Cambisol and Fluvisol, the average B amount recorded was 26.07% in FA, 77.10% in HA, and 2.34% in H. In the Luvisol-2 and Luvisol-3, the average amount of B recorded in FA, HA, and H were 34.38%, 65.11%, and 0.52%, respectively. The B distribution of HA with depth showed an antagonist trend with the FA in all soils as shown in Figure 3. The B associated with FA generally tends to decrease with depth, but the B associated with HA tends to increase with the increase of soil depth and vice-versa. Additionally, the HA fraction exhibited the highest B percentage in all soils, with an exception for the Luvisol-2, where the FA fraction recorded the highest B percentage. The Mann-Whitney U test did not reveal any significant difference in the FA, HA and H between the calcareous and non-calcareous soils. Therefore, the distribution of B in Humic substances was independent of soil land use. Thus, the HA fraction contained the highest percentage of B (mean of 70.69%), the FA fraction a lesser percentage (mean of 27.88%), and the humin recorded the least percentage (mean of 1.43%), independent of soil uses management.

4. DISCUSSION

4.1. Total and available B dynamics

The total B amount varied from 58.78 to 104.65 mg kg^{-1} in the Luvisol-1, Vertisol, Cambisol and Fluvisol (calcareous soils) and from 54.87 to 92.28 mg kg^{-1} in the Luvisol-2 and Luvisol-3 (non-calcareous soils). Indeed, the Luvisol-1, Vertisol, Cambisol and Fluvisol (calcareous soils) are agricultural soils. However, the Luvisol-2 and Luvisol-3 (non-calcareous soils) are forest soils. This is in accordance with Arunkumar et al. (2018), who reported that the total B content in soils varied from 20 to 200 mg kg^{-1}. Therefore, the parent material is considered a dominant factor affecting soil B amount (Nazir et al., 2016; Arunkumar et al., 2018). The correlation analysis (Figure A11 of the Supplementary materials) of total B content showed a positive correlation with silt (r = 0.59) and clay (r = 0.47) contents, and a negative correlation with sand content (r = - 0.66). Our results confirmed with the findings of Arunkumar et al. (2018) and Kumar et al. (2021) who indicated that coarse-textured soils contain less total B compared to fine-textured soil.

The mean available B amount of 0.73 and 1.52 mg kg^{-1} observed in agricultural and forest soils, respectively, would indicate the absence of B deficiency and toxicity. Sun et al. (2019) mentioned that 0.5–2.0 ppm represents the optimal soil B range, whereas lower and higher values indicate deficiency and toxicity. Consequently, no deficiency was revealed in the studied soils. In agricultural soils (calcareous soils), the available B distribution is higher in surface horizons compared to deep horizons. Conversely, the available B distribution recorded in forest soils (non-calcareous) is higher in the deep horizon. Evidence of higher B availability in surface horizons compared with the deep horizon in agricultural soils is related to the high amount of OM content and low $CaCO_3$ content recorded in the surface horizons. These results were supported by other researchers. For example, Barman et al. (2017) reported that the available B was comparatively higher in the surface horizons in agricultural soils of west Bengal. Kumar et al. (2021) observed that available B content decreased with increasing soil depth in agricultural calcareous soil located in north-western India. Therefore the physicochemical soil properties have been identified as affecting B dynamic and distribution in the soil (Prasad et al., 2014; Nath et al., 2018b; Gürel et al., 2019; Padbhushan et al., 2019). Indeed, the available B amount increased with depth in the Luvisol-2 and Vertisol. However, a slight impoverishment was recorded in the sub-horizons and this latter may be explained by a slight increase in the pH level. Even the correlation analysis indicated a significant and negative correlation between available B and pH (r = -0.58). Similar results were reported by Kumar and Babel (2011), who indicated that the available B contents were reduced with an increase in soil pH. The availability of B is mostly related to soil pH and is widely available at a low pH because the adsorption of B increases at high pH (Zhu et al., 2007; Tlili et al., 2019). However, it is frequently leached out of acid, sandy soils. Calcareous soils with a low organic matter content are more susceptible to B deficiency (Nazir et al., 2016; Laik et al., 2021). However, the available B amount decreased with depth in both Luvisol-1 and Cambisol. Nevertheless, a higher content of available B was recorded in the sub-horizons of these both soils and this may be due to the increase of fine fractions (silt and clay percentage). Our results are in line with previous studies, which reported that fine-textured soils often contain more available B than coarse-textured soils (Saleem et al., 2011; Prasad et al., 2014; Dridi et al., 2018; Nath et al., 2018b). Indeed, finer fractions (silt and clay) contribute to improving soil structure and aeration which are favourable conditions for increasing the availability of B (Kumar and Babel, 2011). Whereas, the coarse-textured soils are low in B because they are well-drained (Nath et al., 2018b). Furthermore, Nazir et al. (2016) reported that sandy soils with fine-textured sub-horizons generally do not respond to B in the same manner as those with coarse-textured sub-horizons. It is because fine-textured sub-horizons are expected to retard the vertical movement of B. Thus, a high level of B could be recorded in these sub-horizons caused by a lack of leaching. Available B distribution in the Fluvisol showed a moderate decreasing trend with depth. However, a low value of available B was recorded in the sub-horizon compared to the other horizons and it could be due to the increase in $CaCO_3$ content. The significant and negative correlation of available B with $CaCO_3$ (r = -0.52) confirmed previous studies (Prasad et al., 2014; Reshma et al., 2016; Dridi et al., 2018) which indicated that with an increase in the $CaCO_3$ content of soils, the available B contents decrease. Thus, the B precipitates with $CaCO_3$ and becomes unavailable to the soil solution (Niaz et al., 2007; Dridi et al., 2018). As a result, $CaCO_3$ is an important B adsorption surface in soils (Niaz et al., 2007). The distribution of available B in the Luvisol-3 slightly increased with the depth. But a higher content of available B was recorded in the sub-horizon and could be explained by the important amount of organic matter/organic carbon compared to surface and deep horizons. Although in the present study, no significant correlation between available B and organic matter or organic carbon was established, organic matter is always considered to be the main source of available B when released through mineralization (Kaundal et al., 2014). Thus, we could justify that the B in organic matter is not instantly available to plants in the studied soils.

4.2. B fractions distribution

Our results showed that the readily soluble Rs-B represented only a small percentage of the total B, less than 1.77%. while the Res-B represented the major portion of soil B ranging from 26.67 to 97.53 %. This is in agreement with several studies that observed that regardless of soil and climatic conditions, the Rs-B ranged from 0.16% to 2.68 %, the Spa-B oscillated from 0.14% to 11.9%, the Ox-B varied from 0.16 % to 17 %, the Org-B ranged from 0.56 to 15.6 % and the Res-B varied from 56.1% to 99% of total soil B (Raza et al., 2002; Kaundal et al., 2014; Padbhushan and Kumar, 2015; Kumari et al., 2017; Gürel et al., 2019; Padbhushan et al., 2019; Laik et al., 2021). Our results showed that the contents of B were in the increasing order as Residual B > Oxide bound B > Organically bound B > specifically adsorbed B > Readily soluble B. Our findings are in accordance with Barman et al. (2017) who reported the same order of B extracted by the different forms: Residual B > Oxide bound B ≅ Organically bound B > specifically adsorbed B > Readily soluble B. The correlation among different fractions of B (Figure A2 of the Supplementary materials) demonstrated that the Rs-B was significantly positively correlated with Ox-B (r = 0.37). The Ox-B was significantly positively correlated with Rs-B (r = 0.37), Org-B (r = 0.64) and available B (r = 0.57). Consequently, Rs-B and Ox-B fractions may be available for plant uptake. Our findings are also in agreement with the observations of Barman et al. (2017) and Kumari et al. (2017) who reported a positive and significant correlation among these fractions. Nevertheless, Bhupenchandra et al. (2020) failed to establish a correlation between Ox-B and available B. The significant negative correlations of ox-B with Res-B (r = -0.82) and total B (r = -0.50) were also found by Padbhushan et. (2019) in agricultural soils located in India. The Org-B was significantly positively correlated with Ox-B (r = 0.64) and available B (r = 0.53) but significantly negatively with Res-B (r = -0.63). This is confirmed by Kaundal et al. (2014), the Org-B fraction showed a significant positive correlation with Ox-B and available B in a study conducted in the North-western Himalayas. Similarly, Nath et al. (2018b) found a positive correlation between Org-B and Ox-B in agricultural soils of the Morigaon district of Assam. Yet, Bhupenchandra et al. (2020) failed to establish a correlation between Org-B and available B. Moreover, Padbhushan et al. (2019) established a negative correlation between Org-B and Res-B. The Res-B was significantly negatively correlated with Ox-B (r = -0.82), and Org-B (r = -0.63) but significantly positively with total B (r = 0.85). Res-B exhibited a negative correlation with Rs-B, Spa-B, Ox-B, Org-B fractions, and available B. Therefore, the residual fraction is the non-labile form of B and it doesn't depend on plant B availability and plant B uptake (Padbhushan and Kumar, 2015). This fact was confirmed by the greatest significant correlation observed between residual B and total B (r = 0.95) (Kaundal et al., 2014; Barman et al., 2017). Although the residual fraction was found to be the most dominant fraction, org-B, Spa-B and Rs-B fractions were found to play major roles in the nutrient supply, crop productivity, and nutrient uptake.

4.3. Available B distribution in particle-size fractions

The investigation of available B in particle-size fractions based on the same unit weight revealed that the available B content found in silt fractions was significantly higher than that in sand fractions. The available B content found in the sand fractions was greater than that in the clay fractions. Thus, our results do not support the common theory that finer particle-size fractions, especially clay fractions, should contain more B than the coarser fractions. Moreover, our data agree with the finding of Nazir et al. (2016) who reported that the fact that fine-textured soils retain more B than coarse-textured does not imply that B uptake in clays is greater than in sands. At equal solution B amount, sandy soils contain more available B than clay soils. Thus, our findings are in line with a previous study by Tlili et al. (2019) which investigated the depth B distribution in the different particle-size fractions in Tunisian soils and indicated a considerable contribution of the silt fraction of 52% of the total available B, followed by the sandy fraction (26% of the total available B) and the clay fraction (15% of the total available B) seem to play a less important role respectively. Moreover, silt contains a high amount of B because tourmaline which is the main B-containing mineral present in soils occurs mostly in silt-size particles (Raza et al., 2002). Given that the silt fractions are the intermediaries of soil organic matter turnover and the organic matter is considered to be the main source of available B when released through mineralization, the microorganisms attached to the silt particle can use the organic matter isolated by the silt particle to generate more available B between different particle sizes (Kaundal et al., 2014).

4.4. Total B distribution in humic substances

The investigation of B in humic substances showed that the HA fraction contained the highest percentage of B (mean of 70.69%), the FA fraction a lesser percentage (mean of 27.88%), and the humin recorded the least percentage (mean of 1.43%), independent of soil uses managements. In fact, both HA and FA can form organo-metallic complexes with a variety of essential micronutrients. These complexes promote mineral uptake by the plant and thus a significant increase in nutrient availability. Our finding is in line with Nazir et al. (2016) who pronounced that B associated with humic acids is the main soil B pool for plant growth that is released during the humification process. This is because humic substances are the most important components of soil organic matter, it represents about 60-80% of total soil organic matter (Matuszak-Slamani et al., 2017). Furthermore, our results conformed to the previous study of Zalba et al. (2017), who examined the degree of affinity between humic substances (HA and FA) and essential plant growth macronutrients and micronutrients in the surface horizons with contrasting soil use (forest and agricultural) in Argentina. Indeed, they reported that forest soils contained higher B amounts than the agricultural soils and that HA was more enriched in B than the FA, with 62% of B bound to HA. Moreover, the finding of Karaman et al. (2017) was also in accordance with our results, they showed that HA enhanced the retention and availability of B in the soil. In contrast, our findings are not in agreement with the finding of Pennisi et al. (2010) who investigated B in humic substances (humic and fulvic acids) in the surface horizon of a pinewood located in Ravenna, Italy. The authors reported that B amount measured in humic substances ranged between 65 and 240 µg B g^{-1} organic acid and that the FA is more enriched in B than the HA.

5. CONCLUSIONS

The results of the present study concluded that the available B amount within the selected Tunisian soils depended on soil parent material, land use, and soil characteristics (pH, $CaCO_3$, texture, and organic matter). The available B amount increased with depth in the forest soils (non-calcareous soils), but it decreased with depth in agriculture soils (calcareous soils). The great amounts of available B were recorded in forest soils than in agricultural soils. The total B amount recorded in soils derived from sedimentary rocks was higher than those derived from igneous rocks. The greatest proportion of soil B is present in the Res-B fraction. It is followed by Org-B, Ox-B, Spa-B, and Rs-B fractions, respectively. The smallest B proportion is found in the Rs-B fraction. The results indicated that the various B fractions are in dynamic equilibrium with each other. The available B distribution in the different particle-size fractions (sand, silt, and clay) showed that the silt fractions recorded the most important amount of available B in all the studied soils compared to sand and clay fractions. The B distribution in humic substances showed that HA contains more B than FA.

6. DECLARATIONS

Conflict of interest: The authors have no conflicts of interest to declare that are relevant to the content of this article.

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FIGURE CAPTIONS

Figure 1. Locations of the studied soil profiles: 1 Luvisol-1 (Fernana), 2 Vertisol (Beja), 3 Cambisol (Oued Zarga), 4 Fluvisol (Oued Meliz), 5 Luvisol-2 (Balta), 6 Luvisol-3 (Cap Negro).

Figure 2. Depth available boron distribution in particle-size fractions of the studied soils in northwest of Tunisia.

Figure 3. Depth total boron distribution in fulvic acids (FA), humic acids (HA) and humin (H) of the studied soils in northwest of Tunisia.

TABLE CAPTIONS

Table 1. Main features of the sampling sites in northwest of Tunisia.

Table 2. Mean and (standard deviation) of the physicochemical properties of the studied soils in northwest of Tunisia.

Table 3. Mean and (standard deviation) of total and available boron (B) contents, and relative amount of B fractions of total B amount of the studied soils in northwest of Tunisia.

SUPPLEMENTARY MATERIAL

Figure A1. Correlation matrix between boron (available and total) and soil properties. EC: Electrical Conductivity, $CaCO_3$: Total lime, TOC: Total organic carbon, TN: Total nitrogen, P_2O_5: Available phosphorus, Ca^{2+}: Available calcium, Mg^{2+}: Available magnesium, Na^+: Available sodium, K^+: Available potassium, CEC: Cation exchange capacity, Av. B: available boron, T. B: total boron.

Figure A2. Correlation matrix among readily soluble B (Rs-B), specifically adsorbed B (Spa-B), oxide bound fraction (Ox-B), organically bound fraction (Org-B), residual fraction (Res-B), total B (T. B) and available B (Av. B).

Table A1. Description of the different morphological characteristics of the studied soils in northwest of Tunisia.

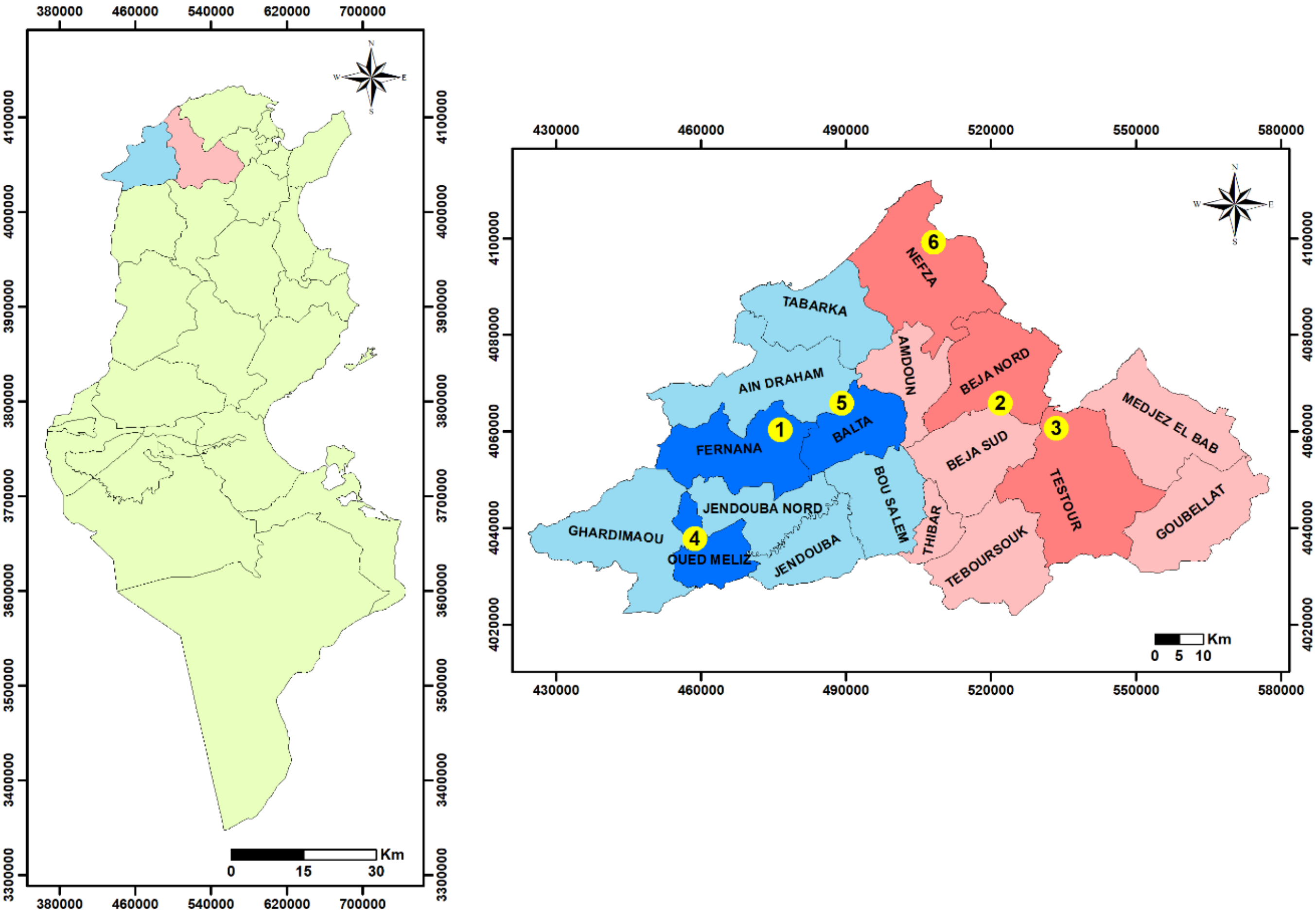


Figure 1. Locations of the studied soil profiles: 1 Luvisol-1 (Fernana), 2 Vertisol (Beja), 3 Cambisol (Oued Zarga), 4 Fluvisol (Oued Meliz), 5 Luvisol-2 (Balta), 6 Luvisol-3 (Cap Negro).

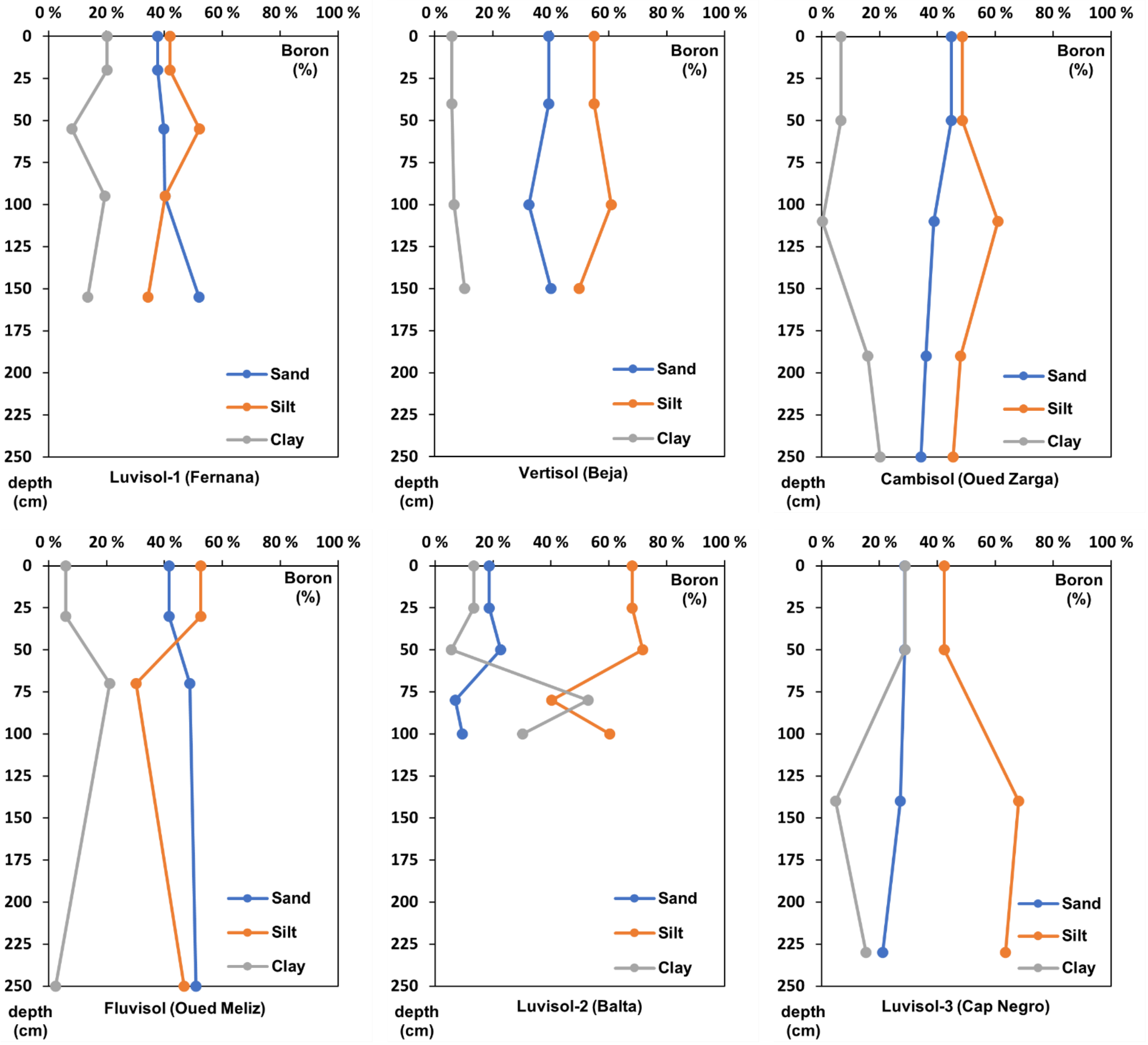


Figure 2. Depth available boron distribution in particle-size fractions of the studied soils in northwest of Tunisia.

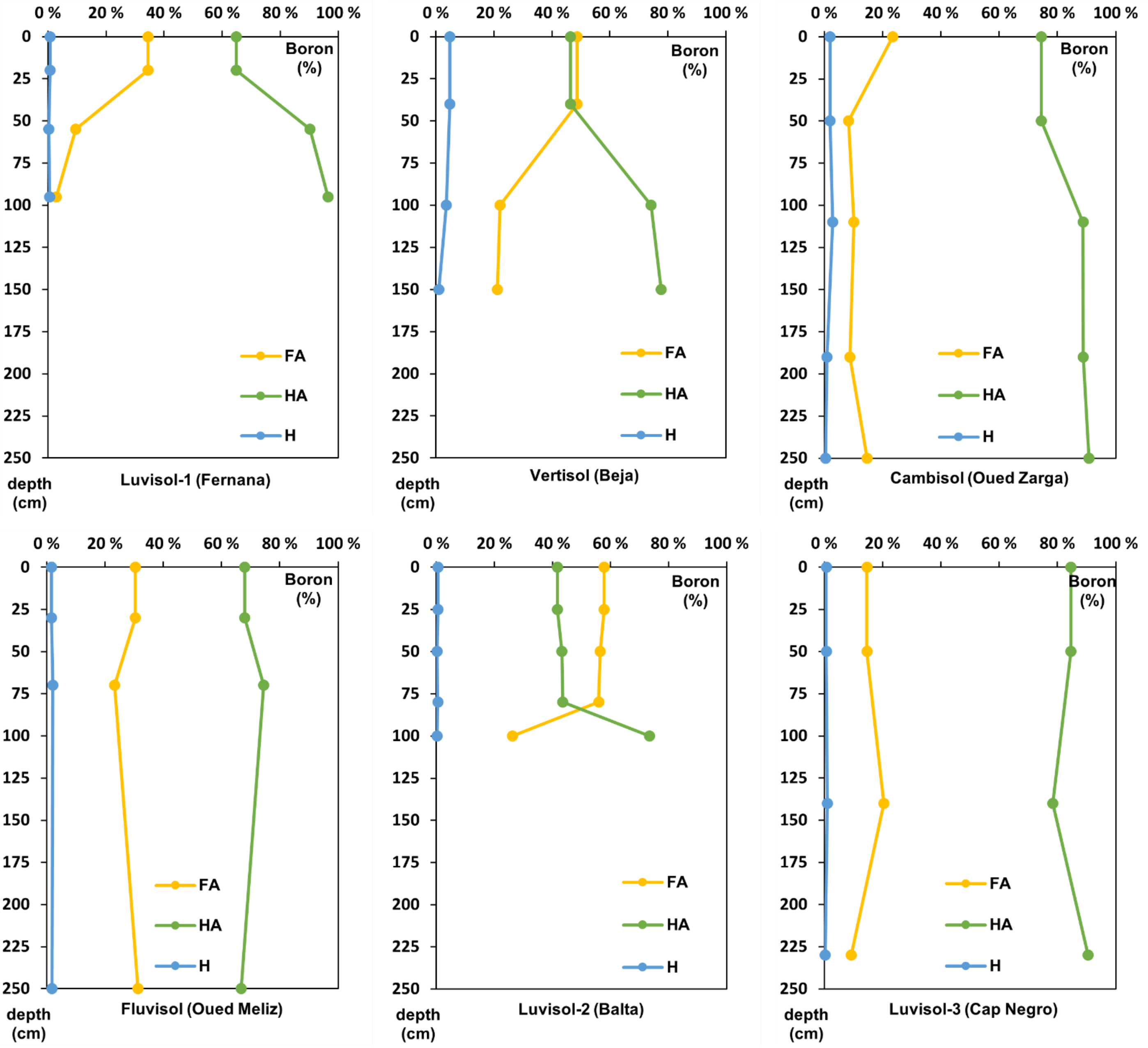


Figure 3. Depth total boron distribution in fulvic acids (FA), humic acids (HA) and humin (H) of the studied soils in northwest of Tunisia.

Table 1. Main features of the sampling sites in northwest of Tunisia.

Site	Latitude	Longitude	Elevation (m a.s.l.)	Bioclimatic zone	Parent material	Land use
Fernana	36°41'16.95''N	8°44'08.26''E	280	Lower humid	Limestone	Agricultural (olive)
Beja	36°44'17.04''N	9°14'46.16''E	223	Sub-humid	Limestone	Agricultural (olive)
Oued Zarga	36°41'26.37''N	9°22'31.57''E	173	Higher semi-arid	Limestone	Agricultural (cereal)
Oued Meliz	36°29'02.00''N	8°32'22.00''E	166	Sub-humid	Limestone	Agricultural (olive)
Balta	36°44'16.81''N	8°52'43.37''E	856	Lower Humid	Sandstones	Forest
Cap Negro	37°02'18.00''N	9°05'31.00''E	83	Lower Humid	Rhyolitic	Forest

a.s.l. = above sea level

Table 2. Mean and (standard deviation) of the physicochemical properties of the studied soils in northwest of Tunisia

Soils	Horizon	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	pH	EC (mS/cm)	$CaCO_3$ (%)	TOC (%)	TN (‰)	C/N	P_2O_5 (ppm)	Ca^{2+}	Mg^{2+}	Na^+	K^+	CEC
															(cmol(+)/kg)		
Luvisol-1	Ap	0-20	49.6 (3.8)	28.5 (1.66)	22 (3.78)	6.7 (0.06)	1.0 (0.3)	2.5 (0.36)	1.1 (0.05)	0.4 (0.08)	24.2 (3.66)	43.6 (4.05)	23.2 (14.86)	1.5 (0.62)	1.8 (0.66)	0.3 (0.06)	26.7 (16.06)
	Bt	20-55	39.7 (3)	32.2 (2.92)	28.1 (1.65)	7.1 (0.14)	0.5 (0.06)	3.9 (0.36)	0.4 (0.04)	0.3 (0.07)	13.9 (2.79)	28 (9.7)	27.6 (6.42)	1.7 (0.69)	1.8 (0.28)	0.2 (0.02)	31.3 (7.42)
	Bk	55-95	56.6 (1.88)	22.5 (1.94)	20.9 (2.03)	7.1 (0.07)	0.7 (0.12)	19.0 (1.49)	0.6 (0.18)	0.4 (0.11)	17.3 (12.17	20.6 (2.86)	28.9 (21.78)	1.6 (0.82)	1.7 (0.97)	0.2 (0.09)	32.5 (23.65)
	Ck	95-155	-	-	-	7.2 (0.16)	0.6 (0.2)	51.2 (0.39)	0.2 (0.01)	0.5 (0.22)	3.7 (1.59)	19.7 (2.12)	29.1 (13.54)	1.8 (0.76)	1.8 (0.61)	0.2 (0.06)	32.8 (14.7)
Vertisol	Ap	0-40	30.7 (7.41)	47.7 (8.08)	21.6 (1.46)	7.1 (0.18)	0.8 (0.09)	32.1 (0.08)	1.1 (0.06)	0.6 (0.16)	17.8 (3.59)	65.2 (1.75)	28.4 (23.65)	1.6 (0.67)	1.9 (1.04)	1.0 (0.08)	32.8 (25.37
	B	40-100	23.2 (2.78)	43.9 (3.16)	32.8 (2.96)	7.2 (0.22)	0.7 (0.03)	27.2 (3.26)	1.4 (0.03)	0.4 (0.17)	34.6 (13.1)	55.6 (3.55)	33 (9.63)	2.2 (1.02)	2.9 (0.42)	0.8 (0.03)	39 (11.1)
	Ck	100-150	27.9 (3.72)	44 (4.23)	28.1 (3.88)	7 (0.16)	1.8 (0.04)	38.6 (1.43)	0.9 (0.07)	0.3 (0.11)	28.3 (13.71	49.9 (5.64)	31.2 (12.6)	2.2 (1.33)	3.5 (0.55)	1.0 (0.04)	37.8 (14.51
Cambisol	Ap	0-50	45.1 (2.64)	34.4 (3.04)	20.5 (3.03)	7.2 (0.06)	1.2 (0.05)	3.0 (0.76)	0.6 (0.02)	0.3 (0.11)	23.5 (9.57)	40.1 (3.14)	14.8 (5.91)	1.7 (0.51)	4.2 (1.62)	0.4 (0.15)	21.0 (8.12)
	Bt	50-110	31.2 (5.66)	36.4 (6.51)	32.5 (5.83)	6.8 (0.09)	0.6 (0.07)	2.2 (0.72)	0.4 (0.02)	0.5 (0.03)	7.9 (0.35)	35.8 (6.01)	16.6 (13.49)	2.4 (1.33)	4.3 (0.57)	0.6 (0.03)	23.9 (15.4)
	Bk	110-190	31.9 (5.07)	42.5 (5.77)	25.7 (5.19)	7.3 (0.26)	0.6 (0.05)	35.6 (0.77)	0.3 (0.08)	0.3 (0.03)	9.0 (2.91)	30.4 (6.05)	26.3 (15.06)	2.3 (1.61)	2.5 (0.66)	0.4 (0.05)	31.6 (17.38
	Ck	190-250	40.1 (6.62)	41.5 (7.36)	18.4 (6.75)	6.7 (0.35)	1.5 (0.02)	48.9 (1.08)	0.2 (0.03)	0.2 (0.1)	6.9 (5.01)	38.7 (6.31)	25.8 (4.3)	2 (0.33)	5.8 (0.16)	0.3 (0.03)	33.8 (4.74)
Fluvisol	Ah	0-30	41.4 (2.67)	25 (2.68)	33.6 (2.78)	7.1 (0.15)	0.9 (0.04)	18.8 (2.89)	0.8 (0.03)	1.2 (0.15)	7.3 (0.71)	26 (1.09)	26.3 (9.28)	1.9 (0.87)	2.5 (0.38)	0.6 (0.03)	31.2 (10.52
	Bss	30-70	23.6 (1.58)	28.7 (1.59)	47.6 (1.7)	6.4 (0.15)	0.8 (0.17)	28.5 (0.06)	0.3 (0.02)	0.4 (0.15)	8.6 (4.57)	35.6 (1.41)	26.3 (4.55)	1.9 (0.42)	4.3 (0.19)	0.3 (0.01)	32.8 (5.15)
	Bss/Css	70-250	28.6 (2.09)	26.2 (2.01)	45.2 (2.24)	6.7 (0.25)	0.9 (0.17)	23.5 (0.72)	0.5 (0.05)	0.6 (0.13)	8.1 (1.08)	22.7 (0.35)	29.5 (10.61)	2.5 (0.89)	4.5 (0.4)	0.4 (0.06)	36.8 (11.87
Luvisol-2	Ah	0-25	45.2 (3.44)	32.3 (3.9)	22.6 (3.93)	5.2 (0.03)	1.0 (0.19)	1.8 (0.36)	4.1 (0.25)	1.4 (0.17)	29.9 (5.59)	31.3 (7.37)	10.5 (1.56)	1.7 (0.74)	2 (0.35)	0.4 (0.07)	14.5 (2.2)
	Bt	25-50	67.5 (2.32)	18.1 (2.49)	14.4 (2.65)	5.9 (0.19)	0.6 (0.21)	1.5 (0.05)	1.4 (0.07)	0.9 (0.23)	16.3 (4.26)	42.9 (8.4)	6.5 (3.7)	1.4 (0.32)	1.8 (0.14)	0.3 (0.02)	10 (4.16)
	BC	50-80	72.2 (4.68)	15 (5.28)	12.8 (5.05)	5.4 (0.03)	0.5 (0.18)	1.5 (0.05)	0.4 (0.05)	0.4 (0.1)	10.0 (3.41)	53 (7.13)	3.9 (1.66)	1.2 (0.85)	1.8 (1.09)	0.4 (0.09)	7.3 (3.26)
	C	80-100	74.7 (2.37)	14 (1.9)	11.3 (2.4)	4.1 (0.34)	0.5 (0.04)	1.5 (0.05)	0.2 (0.04)	0.5 (0.16)	4.2 (1.11)	45.6 (7.69)	2.4 (1.03)	1.2 (0.29)	1.6 (0.14)	0.2 (0.02)	5.4 (1.44)
Luvisol-3	Ah	0-50	25.9 (1.66)	44.2 (1.82)	29.9 (1.93)	5.6 (0.11)	0.7 (0.09)	2.2 (0.72)	0.4 (0.03)	0.9 (0.05)	4.3 (0.55)	14.6 (1.4)	4.5 (2.22)	2.1 (1.62)	4 (0.68)	0.5 (0.04)	11.1 (4.45)
	Bt	50-140	24 (6.71)	39.5 (5.46)	36.5 (6.75)	5.7 (0.1)	0.7 (0.12)	2.2 (0.72)	0.8 (0.06)	0.9 (0.1)	8.3 (1.16)	22.3 (0.7)	5.0 (1.32)	2.0 (1.38)	1.9 (0.57)	0.4 (0.19)	9.3 (3.18)
	C	140-230	29.8 (3.27)	40.1 (3.12)	30.1 (3.4)	5.9 (0.25)	0.8 (0.16)	2.8 (0.04)	0.1 (0.01)	1 (0.04)	0.7 (0.06)	32.6 (4.91)	3.4 (1.11)	2.6 (1.12)	2.3 (0.47)	0.5 (0.03)	8.8 (2.3)

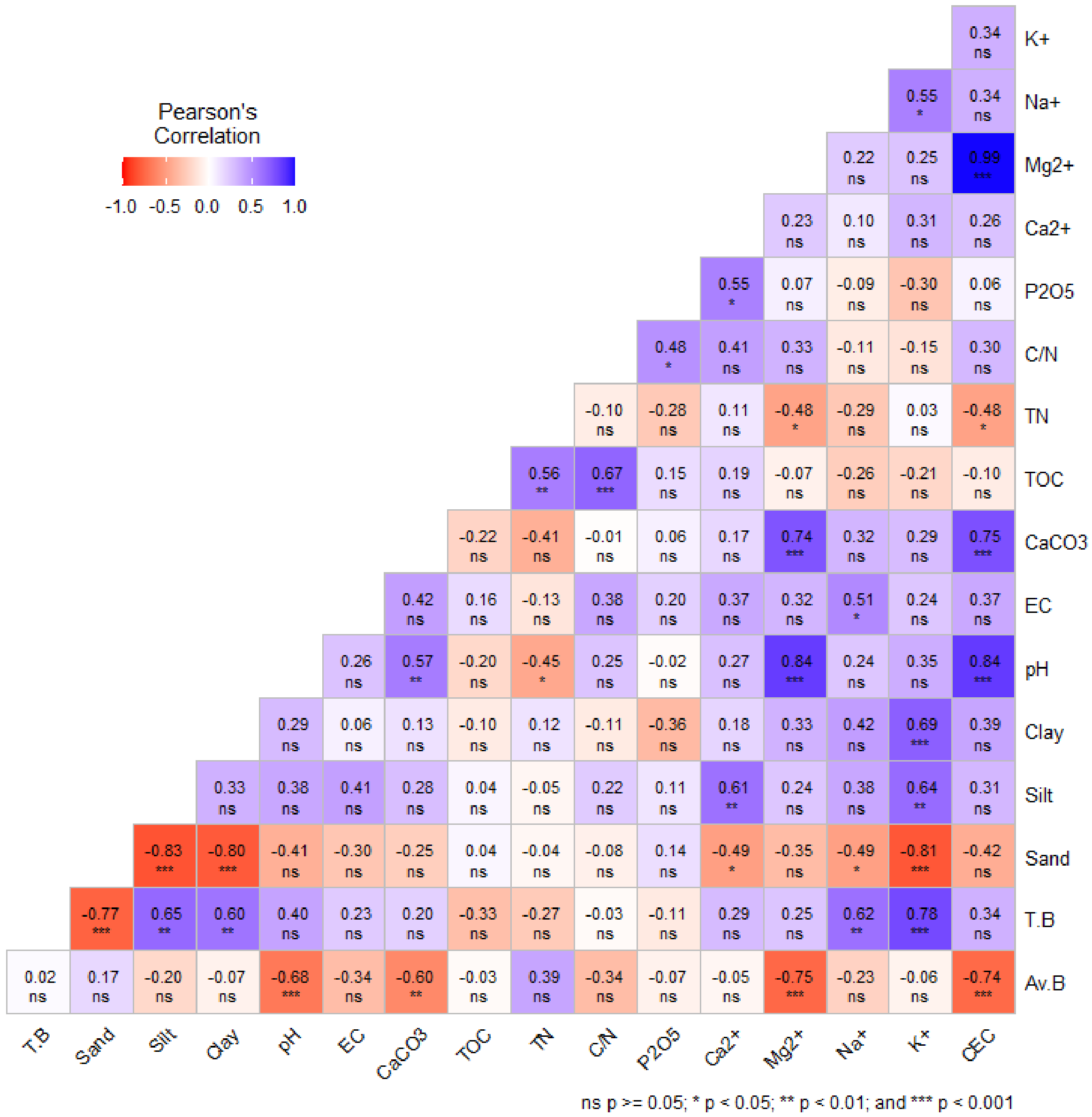
EC: Electrical Conductivity, $CaCO_3$: Total lime, TOC: Total organic carbon, OM: Organic matter, TN: Total nitrogen, P_2O_5: Available phosphorus, Ca^{2+}: Available calcium, Mg^{2+}: Available magnesium, Na^+: Available sodium, K^+: Available potassium, CEC: Cation exchange capacity

Table 3. Mean and (standard deviation) of total and available boron (B) contents, and relative amount of B fractions of total B amount of the studied soils in northwest of Tunisia.

Soils	Depth (cm)	Total B (mg kg^{-1})	Available B (mg kg^{-1})	Rs-B (%)	Spa-B (%)	Ox-B (%)	Org-B (%)	Res-B (%)
Luvisol-1	0-20	73.14 (2.3)	0.5 (0.19)	1.27 (0.4)	0.32 (0.22)	14.09 (0.77)	1.72 (0.4)	82.09 (0.9)
	20-55	68.28 (1.0)	0.61 (0.26)	0.83 (0.26)	1.05 (0.14)	6.87 (0.37)	4.48 (0.25)	86.53 (0.41)
	55-95	71.06 (3.38)	0.46 (0.43)	0.8 (0.25)	0.26 (0.14)	7.48 (0.41)	1.91 (0.2)	89.28 (0.43)
	95-155	58.78 (2.1)	0.21 (0.12)	1.03 (0.32)	0.29 (0.18)	0.21 (0.18)	2.41 (0.13)	96.06 (0.36)
Vertisol	0-40	77.57 (3.67)	0.62 (0.42)	0.72 (0.08)	2.35 (0.06)	0.22 (0.04)	1.86 (0.1)	94.85 (0.24)
	40-100	97.76 (1.49)	0.44 (0.28)	0.54 (0.06)	0.56 (0.03)	0.06 (0.03)	11.36 (0.6)7	87.47 (0.74)
	100-150	83.2 (1.95)	0.68 (0.05)	0.82 (0.15)	0.42 (0.08)	0.13 (0.08)	1.72 (0.09)	96.91 (0.22)
Cambisol	0-50	99.54 (5.58)	1.04 (0.15)	0.54 (0.11)	0.16 (0.06)	7.58 (0.44)	21.22 (1.17)	70.22 (1.17)
	50-110	88.15 (2.1)	1.25 (0.77)	0.64 (0.13)	0.43 (0.07)	8.39 (0.48)	1.48 (0.25)	88.75 (0.65)
	110-190	104.65 (2.3)	1.28 (0.68)	0.67 (0.12)	0.26 (0.07)	0.13 (0.07)	4.75 (0.27)	94.18 (0.38)
	190-250	86.63 (0.67)	0.28 (0.16)	0.45 (0.09)	0.23 (0.05)	0.12 (0.05)	1.66 (0.09)	97.53 (0.17)
Fluvisol	0-30	71.89 (1.45)	1.2 (0.55)	1.45 (0.51)	3.93 (0.26)	0.51 (0.29)	16.71 (0.93)	77.38 (1.41)
	30-70	86.17 (0.71)	0.43 (0.27)	0.64 (0.07)	2.75 (0.07)	0.13 (0.04)	1.67 (0.09)	94.8 (0.24)
	70-250	104.24 (1.6)	1.16 (0.25)	0.86 (0.25)	0.77 (0.14)	0.11 (0.07)	1.37 (0.07)	96.89 (0.25)
Luvisol-2	0-25	56.82 (1.51)	1.19 (0.38)	1.77 (0.6)	1.43 (0.33)	25.23 (0.34)	35.79 (2.05)	35.78 (2.53)
	25-50	54.87 (0.58)	0.82 (0.35)	1.71 (0.54)	1.34 (0.29)	32.04 (0.3)	34.08 (1.96)	30.82 (2.39)
	50-80	58.58 (3.79)	1.92 (0.33)	1.34 (0.32)	2.09 (0.16)	37.77 (0.18)	32.12 (1.87)	26.67 (2.19)
	80-100	61.11 (0.55)	2.03 (0.14)	1.34 (0.35)	0.59 (0.19)	33.91 (0.19)	18.13 (1.04)	46.02 (1.32)
Luvisol-3	0-50	89.86 (2.45)	1.15 (0.67)	0.76 (0.14)	1.54 (0.07)	12.53 (0.74)	6.56 (0.42)	78.16 (0.98)
	50-140	92.28 (2.01)	2.14 (0.51)	1.17 (0.43)	0.77 (0.23)	16.33 (0.9)	21.17 (1.12)	59.99 (1.32)
	140-230	89.67 (1.7)	1.4 (0.51)	0.41 (0.1)	0.97 (0.05)	5.78 (0.33)	14.87 (0.82)	77.77 (0.84)

Rs-B: Readily soluble; Spa-B: Specifically adsorbed; Ox-B: Oxide bound; Org-B: Organically bound; Res-B: Residual.

SUPPLEMENTARY MATERIALS



	T.B	Sand	Silt	Clay	pH	EC	CaCO3	TOC	TN	C/N	P2O5	Ca2+	Mg2+	Na+	K+	CEC
K+																0.34 ns
Na+															0.55 *	0.34 ns
Mg2+														0.22 ns	0.25 ns	0.99 ***
Ca2+													0.23 ns	0.10 ns	0.31 ns	0.26 ns
P2O5												0.55 *	0.07 ns	-0.09 ns	-0.30 ns	0.06 ns
C/N											0.48 *	0.41 ns	0.33 ns	-0.11 ns	-0.15 ns	0.30 ns
TN										-0.10 ns	-0.28 ns	0.11 ns	-0.48 *	-0.29 ns	0.03 ns	-0.48 *
TOC									0.56 **	0.67 ***	0.15 ns	0.19 ns	-0.07 ns	-0.26 ns	-0.21 ns	-0.10 ns
CaCO3								-0.22 ns	-0.41 ns	-0.01 ns	0.06 ns	0.17 ns	0.74 ***	0.32 ns	0.29 ns	0.75 ***
EC							0.42 ns	0.16 ns	-0.13 ns	0.38 ns	0.20 ns	0.37 ns	0.32 ns	0.51 *	0.24 ns	0.37 ns
pH						0.26 ns	0.57 **	-0.20 ns	-0.45 *	0.25 ns	-0.02 ns	0.27 ns	0.84 ***	0.24 ns	0.35 ns	0.84 ***
Clay					0.29 ns	0.06 ns	0.13 ns	-0.10 ns	0.12 ns	-0.11 ns	-0.36 ns	0.18 ns	0.33 ns	0.42 ns	0.69 ***	0.39 ns
Silt				0.33 ns	0.38 ns	0.41 ns	0.28 ns	0.04 ns	-0.05 ns	0.22 ns	0.11 ns	0.61 **	0.24 ns	0.38 ns	0.64 **	0.31 ns
Sand			-0.83 ***	-0.80 ***	-0.41 ns	-0.30 ns	-0.25 ns	0.04 ns	-0.04 ns	-0.08 ns	0.14 ns	-0.49 *	-0.35 ns	-0.49 *	-0.81 ***	-0.42 ns
T.B		-0.77 ***	0.65 **	0.60 **	0.40 ns	0.23 ns	0.20 ns	-0.33 ns	-0.27 ns	-0.03 ns	-0.11 ns	0.29 ns	0.25 ns	0.62 **	0.78 ***	0.34 ns
Av.B	0.02 ns	0.17 ns	-0.20 ns	-0.07 ns	-0.68 ***	-0.34 ns	-0.60 **	-0.03 ns	0.39 ns	-0.34 ns	-0.07 ns	-0.05 ns	-0.75 ***	-0.23 ns	-0.06 ns	-0.74 ***

ns p >= 0.05; * p < 0.05; ** p < 0.01; and *** p < 0.001

Figure A1. Correlation matrix between boron (available and total) and soil properties. EC: Electrical Conductivity, $CaCO_3$: Total lime, TOC: Total organic carbon, TN: Total nitrogen, P_2O_5: Available phosphorus, Ca^{2+}: Available calcium, Mg^{2+}: Available magnesium, Na^+: Available sodium, K^+: Available potassium, CEC: Cation exchange capacity, Av. B: available boron, T. B: total boron.

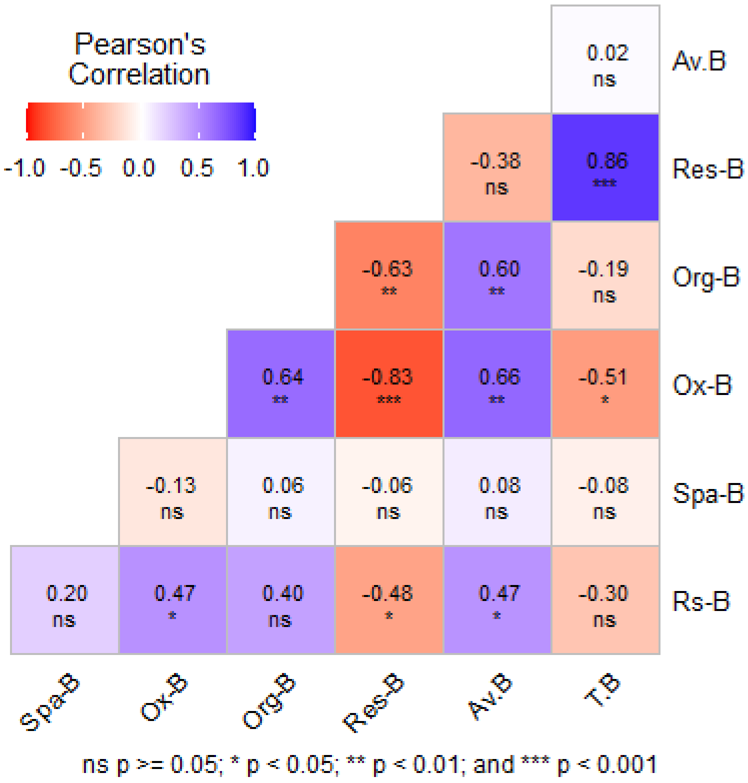


Figure A2. Correlation matrix among readily soluble B (Rs-B), specifically adsorbed B (Spa-B), oxide bound fraction (Ox-B), organically bound fraction (Org-B), residual fraction (Res-B), total B (T. B) and available B (Av. B).

Table A1. Description of the different morphological characteristics of the studied soils in northwest of Tunisia.

Pedon	Horizon	Depth (cm)	Colour [1]	Boundary [2]	Texture [3]	Structure [4]	Consistence [5]	Roots [6]	Biological	$CaCO_3$ [8]	Rock fragmen
Fernana Luvisol-1	Ap	0-20	7.5 YR	C W	L	2/SA/	HA,	2	M	N	3 CS
	Bt	20-55	10 YR	C I	CL	2/AB/	SHA,	1	F	MO	1 FM
	Bk	55-95	10 YR	D I	SCL	2/SB/F	SHA,	2	F	SL	5 CS
	Ck	95-	10 YR	-	-	1/MA	SO, SSS	-	N	EX	0
Beja Vertisol	Ap	0-40	10 YR	C W	L	1/LU/	SO, SST	3	M	EX	2 MC
	B	40-	10 YR	C W	CL	2/SB/	SHA,	3	C	ST	1 F
	Ck	100-	10 YR	-	CL	2/AB/F	SHA,	1 F	F	EX	6 L
Oued Zarga Cambisol	Ap	0-50	5 YR	C S	L	2/GR/F	SHA,	4	M	N	1 MC
	Bt	50-	5 YR	C S	CL	2/SB/	SHA,	3	C	N	3 FM
	Bk	110-	5 YR	C W	L	3/GR/	HA,	0	F	ST	2 BL
	Ck	190-	5 YR	-	L	1/AB/F	VHA,	1 F	N	EX	4 CS
Oued Meliz Fluvisol	Ah	0-30	10Y	C W	CL	1/LU/F	SO,	4	M	ST	0
	Bss	30-70	2.5YR	C S	C	2/MA	SHA,	3	C	EX	0
	Bss/Css	70-250	2.5 Y 5/3	-	C	3/AB/FM	HA, SST	0	N	ST	0
Balta Luvisol-2	Ah	0-25	2.5Y	C W	L	2/GR/F	SO, SSS	3	M	N	2 MC
	Bt	25-50	2.5Y	C W	SL	2/LU/	SHA,	2	C	N	1 F
	BC	50-80	7.5 YR	C W	SL	1/GR/	SHA,	1	F	N	1 F
	C	80-	10YR	-	SL	1/MA	SHA,	0	N	N	0
Cap Negro Luvisol-3	Ah	0-50	7.5 YR	G S	CL	1/GR/	SO, SST	3	M	N	1 FM
	Bt	50-	5 YR	C W	CL	2/LU/F	SHA,	2	M	N	3 MC
	C	140-230	7.5 YR 6/6	-	CL	3/MA/VF	SO, SST	1 M	F	SL	4 BL

[1] **Colour:** moist according to the Munsell Soil Color Chart (1954 edition); [2] **Boundary**: C = Clear, G = gradual, D = Diffuse, S = smooth, W = wavy, I = irregular; [3] **Texture**: L = loam, C = clay, CL = clay loam, SCL = Sandy clay loam, SL = Sandy loam; [4] **Structure**: 1 = weak, 2 = moderate, 3 = strong, LU = lumpy, GR: granular, SB = subangular blocky, AB = angular blocky, MA = massive, SA = Subangular and angular blocky, VF - Very fine, FI = fine, ME = medium, CO = coarse, FF = Very fine and fine, VM = Very fine to medium, FM = Fine and medium, MC = Medium and coarse; [5] **Consistence** (dry): SO = soft, SHA = slightly hard, HA = hard, VHA = very hard, NST = Non-sticky, SST = Slightly sticky, SSS - slightly sticky to sticky; [6] **Roots**: 0 = absent, 1 = very few, 2 = few, 3 = common, 4 = many, VF = very fine, F = fine, M = medium, FF – very fine and fine, FM – Fine and medium, MC – Medium and coarse; [7] **Biological activity**: N = None, F = Few, C = Common, M = Many; [8] **$CaCO_3$**: N = non-calcareous, SL = Slightly calcareous, MO = Moderately calcareous, ST = Strongly calcareous, EX = extremely calcareous; [9] **Rock fragments**: 0 = None, 1 = Very few, 2 = few, 3 = Common, 4 = Abundant, 5 = Dominant, 6 = Stone line, F - Fine gravel, L - Large boulders, FM - Fine and medium gravel, MC - Medium and coarse gravel, CS - Coarse gravel and stones, BL - Boulders and large boulders.