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CASE STUDY

Boron adsorption in semiarid Mediterranean soils under the influence of background electrolytes

S. Fatnassi[1,2*], M.B. Almendro Candel[3], J. Navarro Pedreño[3], I. Gómez Lucas[3], M. Hachicha[2]

[1] Department of Geology, Faculty of Sciences of Tunis, University of Tunis El Manar, 2092 El Manar, Tunis, Tunisia

[2] National Institute of Rural Engineering, Waters and Forest, Carthage University, 2080 BP 10 Ariana, Tunisia

[3] Department of Agrochemistry and Environment, Miguel Hernández University of Elche, Avd.de la Universidad SN, 03202 Elche, Alicante, Spain

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ABSTRACT

BACKGROUND AND OBJECTIVES: Boron is a micronutrient of high importance, both for plant development and normal growth. The range between boron deficiency and toxicity is very narrow, which makes boron unique among the essential micronutrients. Boron adsorption is one of the most important factors determining the release and fixation of this micronutrient, though its adsorption has not been widely studied in semiarid Tunisian soils. This study aims to improve knowledge of B adsorption process in calcareous salt-affected soils in semiarid areas.
It equally focuses on the type of cation (monovalent and divalent) in function of the soil texture and time of shaking. These three latter factors influence boron adsorption, which also influence the availability for plants.
METHODS: A study was carried out on boron adsorption at different shaking time intervals (1, 3, 6 and 9 hours) in two soils of different textures in the absence and presence of different background electrolytes solutions (0.02 N $CaCl_2$, 0.02 N $MgCl_2$, 0.02 N sodium chloride and 0.02 N potassium chloride.
FINDINGS: The soil-A (clay loam) adsorbed more boron than soil-B (sandy loam). Boron adsorption was the highest in Soil-A under the presence of potassium chloride, close to the mean values given when using calcium chloride. In Soil-B, it was found with calcium chloride background electrolyte. Minor boron adsorption was observed in both soils when boric acid solution was used without background electrolytes. Adsorbed boron showed significant differences with the shaking time in all treatments used with background electrolytes solutions, except for boron solution treatment without background electrolyte in both soils. As a comparison of divalent and monovalent cations, boron adsorbed content was higher with the solution containing calcium than in sodium chloride solution, due to the fact that calcium carbonate is an important boron adsorbing surface.
CONCLUSION: This study reveals that the best conditions for maximum boron adsorption are defined by calcium chloride background electrolyte in this type of soil in a determined shaking time interval of 3 hours. This causes a low rate of boron assimilated by plants, which leads to the decrease of the crop yield and the agricultural production, and subsequently hurt the Tunisian national economy.

NUMBER OF REFERENCES	NUMBER OF FIGURES	NUMBER OF TABLES
62	4	5

*Corresponding Author:
Email: *salmapro14@gmail.com*
Phone: +216 5596 9642
ORCID: 0000-0002-2017-1056

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INTRODUCTION

Boron (B) is an essential oligo-element required for the growth of plants (Wimmer *et al*., 2019). The development of floral organs and the elongation of pollen tubes are hampered by a low availability of B in soils, resulting in a crop yield loss (Shorrocks, 1997). Boron is unique among the essential micronutrients because it is presented as nonionized boric acid (H_3BO_3) over the pH range suitable for the plant growth (Arora and Chahal, 2007) and B uptake is the result of the passive assimilation of undissociated boric acid (Hu and Brown, 1997). For B vegetal-soil systems, the value between insufficiency and toxicity is the narrowest among important micronutrients (Su and Suarez, 2004; Tariq and Mott, 2006; Hilal *et al*., 2011; Abu-Dabaan and Al-Najar, 2018; Brdar-Jokanović, 2020) which makes B particular among all primordial nutrients. According to Tariq and Mott (2006), Some other elements such as potassium (K), calcium (Ca), magnesium (Mg) and sodium (Na) disponibility are affected by B deficiency and toxicity apart from crop yield. Hence, B content must be monitored frequently in soil, as its management is very critical. Boron toxicity is a far more difficult issue to manage than deficiency (Reid, 2004). Brdar-Jokanović (2020) highlighted that fertilization could be a solution for B deficiency problematics, contrarily to B toxicity which could be ameliorated using effective procedures. The majority of the world's agricultural soils contain 5–30 mg/kg of total B (determined by total digestion of air-dried soil at neutral pH). Understanding the B adsorption on soil process is necessary, as plants react to the B activity in soil solution. Soluble B availability is governed by sorption-desorption processes of this micronutrient, acting as source for plant uptake in soil solution (Chen *et al*., 2002; Bhuyar *et al*., 2020). B added to soils is adsorbed to a variable extent and an equilibrium exists between B in the solid and liquid phases (Bhupenchandra *et al*., 2019). In this regard, these authors indicate that the adsorption of B is one of the most essential factors identifying the release and fixation of applied B and thus deciding the efficiency of B fertilization. Boron mobility can be very restricted for plants, which can provoke deficiency (Brown and Shelp, 1997). Boron deficiency is a widespread issue in relatively humid areas, especially in sandy soils (Santos *et al*., 2020). On the other hand, toxic levels of this element have been reported frequently in arid zones due to anthropic activity such as fertilization and irrigation (Santos *et al*., 2020). The data on B concentrations in sediments have been widely used as paleosalinity indicators (Mattigod *et al*., 1985; Kot, 2009). According to Schwager-Guilloux (2014), coastal soils can be rich in B since seawater is relatively well provided in this element (B content is approximately 4.7 mg/L). For this reason, B frequently exceeds the plant's requirement in arid and semiarid environments due to low drainage, and in agricultural soils close to coastal areas due to the intrusion of B-rich seawater in fresh aquifers or as a result of dispersion of seawater aerosol. Global releases of elemental B through weathering, volcanic and geothermal processes are also relevant in enriching B concentration in some areas (Landi *et al*., 2019). Boron adsorption is impacted by soil pH, clay percentage, and organic matter (Ramos *et al*., 2021). In fact, B has been identified as one of the elements to be defined in irrigation water quality since the 1950s by Richards (1954) and included in the FAO guidelines (JECFA, 1974) for the use of water for crop irrigation. It has also been considered in the use of treated wastewater (TWW) both by the World Health Organization (WHO, 2006) and in Tunisian standards (Table 1) for the discharge of these waters into the aquatic environment and the sea NT 106.02 (Errais *et al*., 2010), the agricultural use of these waters NT 106.03 (Errais *et al*., 2010), and for drinking water NT 09.14 (Jalal and Ezzedine, 2019). Generally, B mobility varies greatly from freely mobile to very restricted one according to the soil and the plant species (Brown and Shelp, 1997; Boaretto *et al*., 2011). Plants are very specific regarding their B tolerance wherefore irrigation water should not contain more B than required for crop development to avoid toxicity (Maas, 1986; Corwin and Yemoto, 2020). Due to their relative sensibility towards B, the irrigation water used for cereals should not contain more B than 300-400 µg/L. Citrus fruits such as lemon can show higher vulnerability (< 0.5 mg/L) towards B concentration (Nicolás *et al*., 2016). Consequently, the management of this micronutrient in soil has become recently a worldwide agricultural issue. The most recent similar studies often investigate the B adsorption, by the same methodology. The latter consists in shaking the soil for 24 h or 20 h, with a determined volume and concentration of a background electrolyte solution, containing different concentrations of boric acid.

Table 1: Boron Thresholds values and recommendations for different water uses and countries.

Medium	Values (mg/L)	Countries	References
Groundwater	1.0	Europe	(Albrecht, 2013)
Drinking water	2.4	Tunisia	(Jalal and Ezzedine, 2019)
Drinking water	0.5	Worldwide	(Hjelm *et al.*, 2019)
TWW for irrigation	3.0	Tunisia	(Errais *et al.*, 2010)
TWW discharged to seawater	20.0	Tunisia	(Errais *et al.*, 2010)

For instance, Terraza Pira *et al*. (2018) accomplished the B adsorption isotherms using 25 mL of seven solutions of different B concentrations (0, 2, 4, 8, 16, 32, and 64 mg/L in 0.01 M CaCl), which were added independently to 5 g soil and shaken for 20 h in a reciprocal shaker. However, the current study aim does not focus on B adsorption in soil in the presence of different B concentrations, in one shaking time interval with one cation, as mentioned in the recent studies. Actually, it concentrated on B adsorption in soil in function of different parameters effect: the type of cations in soil solution (divalent or monovalent), the soil texture and the shaking time (1, 3, 6 and 9 hour). Therefore, there are hardly any works with the same research objectives. As a matter of fact, there is a lack of investigations on boron adsorption in the case of calcareous salt-affected soils in semiarid areas particularly under the combination of various background electrolytes and shaking time effect during the quantification in laboratory. Moreover, among the metal minor elements, B is the element whose mobility increases in a basic environment. This is the case of Tunisian soils rich in limestone, which is an additional argument to highlight the importance of B in semiarid Mediterranean regions. The global aim of the study is to improve knowledge of B mobility and interaction with other chemical elements in calcareous salt-affected soils in semiarid areas. The aim of the current study is to focus on the type of cation (monovalent and divalent) that can favor the B adsorption in function of the soil texture and time of shaking. This also influence the availability of B for plants. Hence, B content must be monitored frequently in soil, as its management is very critical. This study contribution consists in providing the optimal conditions in this type of soil (type of cation and exact shaking time interval) for maximum boron adsorption. This affects the B amount assimilated by plants, which influence the crop yield and the agricultural production. This study has been carried out in Tunisia, within the research laboratory Valorization of non-conventional waters in the National Research Institute of Rural Engineering, Waters and Forests (INRGREF) for the field activities and the chemical analysis in 2018, and in Spain, in 2019, within the research laboratory at the University of Miguel Hernandez of Elche for the experimental and chemical analysis.

MATERIALS AND METHODS

The literature review highlighted the importance of B sorption-desorption processes, which dominate B availability and thus provide a source for plant uptake in soil solution. Although, there are few studies on boron adsorption in the case of calcareous salt-affected soils in semiarid areas. This context led us to hypothesize that understanding B adsorption in this type of soil is necessary, under several parameters effects such as the background electrolytes type, soil texture and shaking time. Previous studies have not attempted to demonstrate the combination effect of different background electrolytes and time of shaking intervals in the same time on B adsorbed amounts, particularly in this type of soil. The study was carried out with two Fluvisols (Sarmast *et al.,* 2015), with different textures, in order to study the adsorption of B in the soil of Cebala Borj Touil perimeter (Fig. 1).

Description of the study area and context

The sites are located at the perimeter of Cebala Borj-Touil (Fig. 1), Tunisia's most important agricultural area irrigated by treated wastewater (3200 ha). It is in the suburbs of Tunis (36°50 N; 9°75 E) in northeastern Tunisia. This area has been irrigated with treated wastewater (TWW) since 1989. These wastewaters generated from urban activities are treated at the

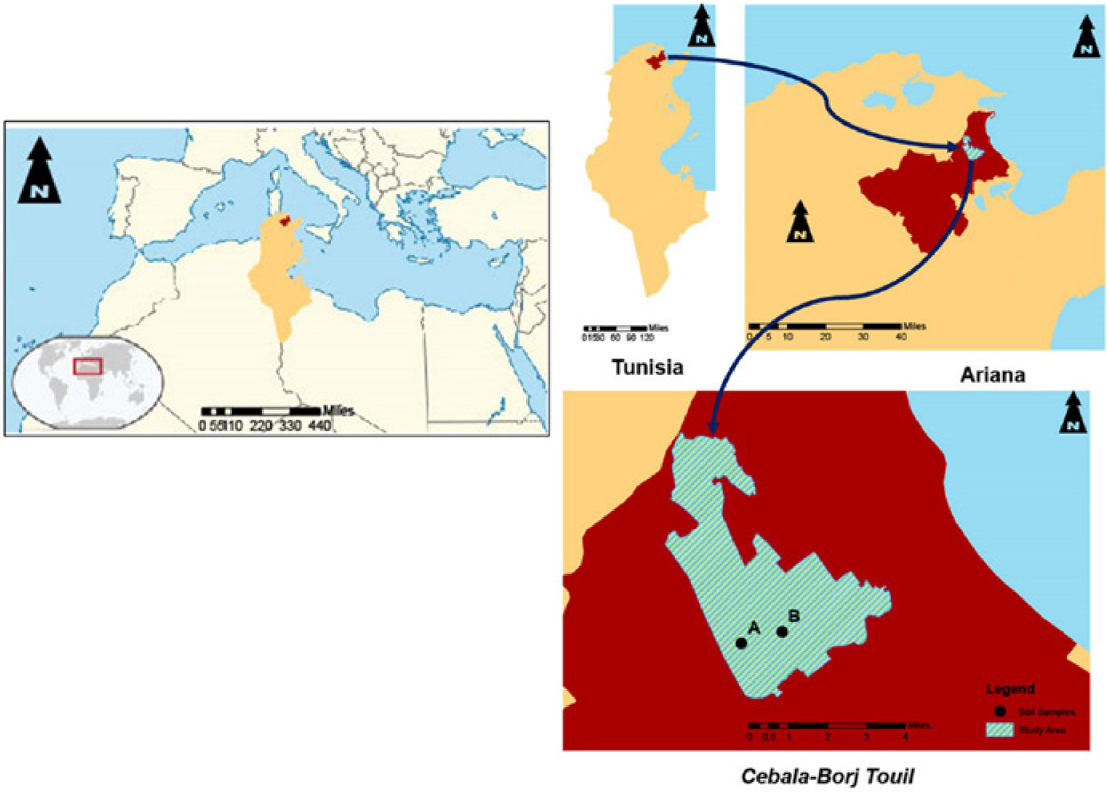

Fig. 1: Geographic location of the study area in northern Tunisia and localization of soil samples in Cebala Borj Touil perimeter

secondary level and available to agricultural and farm irrigation. The effluents were supplied by the outflow of three Great Tunis wastewater treatment plants (Choutrana, Cherguia, and north coast). The main TWW chemical characteristics are mentioned in the Table 2. The pH mean value of irrigation water varies from neutral to slightly alkaline during the summer irrigation cycle. The salinity of TWW (Ecw) is moderate with an average of 4.54 dS/m. The chemical facies is alkaline with a dominance of Na^+ cations and Cl^- anions. B concentration with a mean value 0.75 mg/L remains fairly constant over time. It is bordered on the north by the Mejerda River. The climate is semiarid, with a wet season from September to May and a dry season from June to August. The average annual rainfall is estimated at 470 mm (Dahmouni *et al.,* 2018) with an average annual evapotranspiration of 1400 mm (Khaskhoussy *et al.,* 2015). The region is characterized by a shallow saline water table ranging from 0.5 to 7.6 m. The Cebala Borj-Touil drainage system comprises of an open ditch network that covers the whole region (Dahmouni *et al.,* 2018). The land use differs depending on the season. In winter, cereals and fodders crops as wheat and alfalfa are cultivated, whereas in summer, maize and sorghum. Irrigation is mainly used during hot season for maize and sorghum.

Soil analysis

Soil samples were taken in two agricultural fields situated in the middle of the region. Both samples were air dried and sieved (2 mm) to prepare them for the analysis and laboratory experiment. The soils, Soil-A and Soil-B, selected by their difference in texture and being representative of the area, are respectively clay loam and sandy loam soils (Table 3). The soil texture was determined by using the Robinson pipette method after oxidation of the organic matter with H_2O_2 and particle dispersion with hexametaphosphate solution (NF [French norm]

Table 2: Main treated wastewater chemical characteristics

Descriptive statistics	pH	Ecw (dS/m)	Cl^- (meq/L)	HCO_3^- (meq/L)	SO_4^{2-} (meq/L)	Ca^{2+} (meq/L)	Mg^{2+} (meq/L)	K^+ (meq/L)	Na^+ (meq/L)	B (mg/kg)
Average	7.27	4.54	32.15	6.5	10.03	6.5	10	1.24	28.48	0.75
Min.	6.96	3.57	22.56	4	5.52	5	7.5	1.07	20.06	0.73
Max.	7.6	5.36	42.3	9	15.1	7.5	15	1.39	39.11	0.77

Table 3: Main soil properties

Soil	Clay (%)	Silt (%)	Sand (%)	pH	EC (dS/m)	$TCaCO_3$ (%)	OM (%)	Hot water extractable B (mg/kg)
A	36.0	42.2	21.8	8.0±0.1	3.1±0.2	35.4±7.3	1.36±0.03	1.2±0.1
B	19.0	14.8	66.2	7.9±0.1	7.6±0.6	45.7±2.2	0.75±0.06	1.4±0.1

± is followed by the standard deviation (SD).

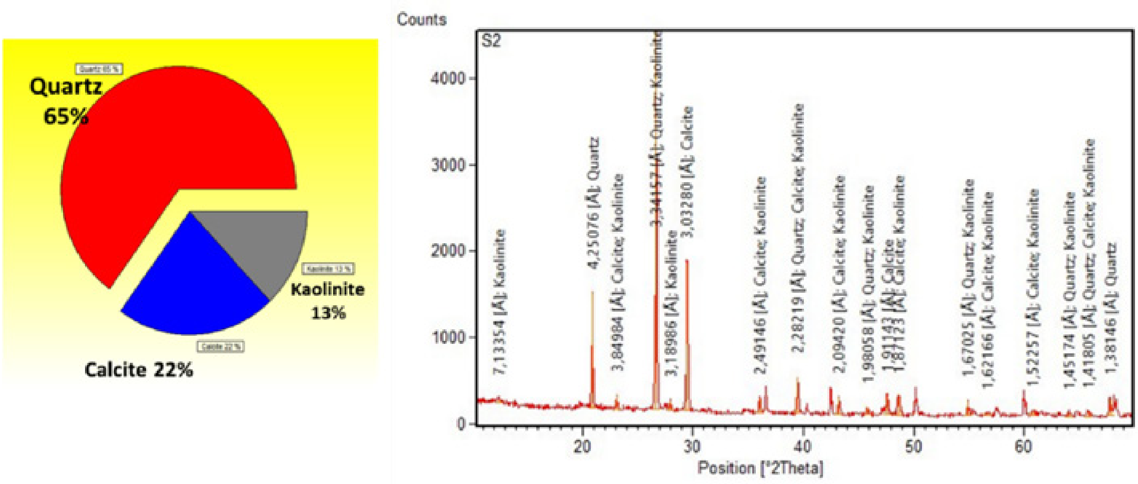

Fig. 2: X-ray diffract metric analysis of the studied soil

X31-107). The X-ray diffractometric analysis showed that the mineralogical composition of the soil is as follows: 65% of quartz, 22% of calcite and 13% of kaolinite (Fig.2). In Fig. 2, the soil X-ray diffractometric pattern presents a high signal for the diffraction lines of intensity relevant for quartz. The wide lines at 21, 27, 39 and 46° in 2θ are characteristics of quartz . Calcite was present in soil, with 23, 30, 36, 44, 47 and 61° in 2θ. In addition, Kaolinite was observed at a low intensity with other elements (quartz and calcite) in many lines (at 3, 23, 28°... in 2θ). The soil pH was measured with a pH meter in water extraction (ISO 10390). The salinity was measured determining the electrical conductivity (EC) in the soil aqueous extract (ISO 11265). The total equivalent calcium carbonate ($TCaCO_3$) was estimated by using the volumetric method and the attack of the soil sample with hydrochloric acid (NF ISO 10693) (Jerbi *et al.,* 2020). Organic matter was estimated following the loss on ignition method (Benbi, 2018). Initial available B concentration in soils was determined after hot water extraction with the Carmine method (Sah and Brown, 1997; Pena-Pereira *et al.,* 2020). The main differences observed in these soils were in texture, electrical conductivity, total equivalent calcium carbonate and organic matter. The presence of a higher percentage

Table 4: Cations and anions availability in the soils

Soil	Cl^- (meq/L)	HCO_3^- (meq/L)	SO_4^{2-} (meq/L)	Ca^{2+} (meq/L)	Mg^{2+} (meq/L)	K^+ (meq/L)	Na^+ (meq/L)
A	12.69	5.00	14.76	10.00	5.00	0.28	16.11
B	59.22	3.17	11.48	13.33	14.83	0.94	45.68

of clay fraction in Soil-A, and sand fraction in Soil-B would determine their physical characteristics. The ionic composition in the soil-B was dominated by the anion Cl^- and the cation sodium Na^+. In soil-A, it was dominated by the anion SO_4^{2-} and the cation Na^+ (Table 4).

Experimental design on B adsorption in soils

The B adsorption experimental design was based on previous studies (Tamuli *et al.,* 2017). Soil samples (8 g air-dry soil taken in each tube) with 4 replications were disposed into 50 mL polypropylene centrifuge tubes with 16 ml of solution (ratio soil-solution 1:2 w/v) containing 40 mg/L B as boric acid (H_3BO_3). They were shaken under controlled temperature conditions (20ºC) for 1, 3, 6 and 9 hours (h) by using a wrist action laboratory shaker (200 oscillations/min). The following treatments (boron solution-soil interaction) were applied: B solution without background electrolyte (TBo) or with background electrolytes: 0.02 N $CaCl_2$ (TBCa), 0.02 N $MgCl_2$ (TBMg), 0.02 N NaCl (TBNa) and 0.02 N of KCl (TBK). Although the accompanying anion was the same for all the electrolytes, chloride, there were small differences in the pH of the solutions due to the interaction between components and water (ionic strength): 6.5, 6.5, 5.7, 7.3 and 6.6 respectively. The pH of all treatments was close to 6.5 although major differences were observed in the case of TBMg (pH=5.7) and TBNa (pH=7.3). The B in the solution, after shaking time, was measured by the colorimetric method Azomethine-H (Sah and Brown, 1997; Pena-Pereira *et al.,* 2020). The spectrophotometer used was T80 (a high-performance double beam spectrophotometer). The B detection limit in the used method was 0.05 mg/L. The difference between initial concentration and the final concentration in the solution after the interaction with soil, gave the amount of B adsorbed by soil.

Statistical analysis

Descriptive statistics (mean value and standard deviation SD), Student's t- test and one- and two-ways ANOVA test were used to determine the statistical differences between samples. For the samesoil (A or B) and treatment, mean values with a letter (a, b, c), and those with different letters indicated statistical differences by using Student's t-test at $p<0.05$. For the ANOVA test comparing the effect of shaking time and the effect of background electrolyte, statistical differences are represented by using stars with the following meaning: * ($p<0.05$), ** ($p<0.01$) and *** ($p<0.001$), and no significant differences (NS).

RESULTS AND DISCUSSION

A summary of the results concerning the B adsorption in soil-A and soil-B at different time of shaking are shown in Table 5.

Soil B adsorption

Considering the divalent cations Ca and Mg, in the case of TBCa, B adsorbed in Soil-A increased from 1 h to reach a maximum after 6 h of shaking (25.4 mg B/kg soil), then decreased slightly at 9 h shaking. In Soil-B, B content adsorbed by soil increased starting from 1 h of shaking time to 3 h. It decreased after 6 h of shaking and finally increased again and reached a maximum value after 9 h of shaking (19.3 mg B/kg) but without statistical differences between 6 and 9 h of time of shaking (T test). The B adsorbed showed higher values in Soil-A than in Soil-B. In the case of TBMg, B adsorbed in Soil-A increased from 1 h to reach a maximum after 6 h of shaking (23.9 mg B/kg). In Soil-B, B content adsorbed by soil increased starting from 1 h of shaking time to 3 h, then decreased slightly and reach the maximum value at 9h (17.6 mg B/kg). Considering NaCl and KCl as background electrolytes, in both cases, the B adsorbed increased progressively in Soil-A from 1 h to 6 h of shaking, then slightly decreased at 9 h of shaking, but without statistical differences. In Soil-B, B adsorbed showed a similar behavior. As it happened in all the previous background electrolyte experiments with divalent cations, B adsorbed

Table 5: B adsorbed (mg B/kg soil), standard deviation, T test and ANOVA 1 and 2 ways in the two soils considering all the treatments (TBCa, TBMg, TBNa, TBK and TBo) and time of shaking

Treatment		TBCa		TBMg		TBNa		TBK		TBo		ANOVA 1 way (background electrolyte effect)
	Shaking time (h)	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	
Soil A	1	23.5^{c}	0.72	21.0^{b}	0.78	23.2^{c}	0.69	26.3^{bc}	0.92	18.4^{a}	0.57	***
	3	24.0^{b}	0.35	21.9^{b}	1.03	24.2^{b}	0.25	27.8^{b}	0.36	18.5^{a}	0.67	***
	6	25.4^{a}	0.50	23.9^{a}	0.85	26.3^{a}	1.39	28.9^{a}	0.64	19.6^{a}	0.65	***
	9	24.9^{ab}	0.58	23^{ab}	1.16	23.8^{bc}	1.53	25.4^{c}	0.77	18.8^{a}	0.36	***
ANOVA 1 way (time effect)		**		**		*		***		NS		ANOVA 1 way (background electrolyte effect)
ANOVA 2 ways (time vs background electrolyte)		***		***		***		***		***		
Soil B	1	17.0^{b}	0.88	14.2^{b}	0.41	15.8^{b}	0.59	15.4^{a}	0.12	12.0^{a}	0.51	***
	3	19.1^{a}	0.93	17.1^{a}	0.95	15.8^{b}	0.59	18.6^{a}	1.21	12.2^{a}	0.86	***
	6	18.6^{a}	0.48	16.6^{a}	0.63	18.2^{a}	0.78	17.3^{ab}	0.79	12.4^{a}	0.30	***
	9	19.3^{a}	0.62	17.6^{a}	0.57	18.2^{a}	0.65	17.0^{b}	0.71	12.8^{a}	0.23	***
ANOVA 1 way (time effect)		**		***		***		**		NS		
ANOVA 2 ways (time vs background electrolyte)		***		***		***		***		***		

Different lowercase letters indicate significant differences among the different time of shaking at $P<0.05$ level and at the same treatment.
NS *, **, and ***indicate not significant, significant at $P < 0.05$, $P < 0.01$, and $P < 0.001$, respectively.

showed greater values in Soil-A than in Soil-B. Concerning boric acid solution without background electrolyte, the B adsorbed showed close values and it is independent of the time of shaking. In Soil-B, B adsorbed increased progressively from 1 h to reach the maximum at 9 h of shaking, but without significant differences. The ANOVA test confirmed that no effect associated with shaking time was noticed. However, B adsorbed showed higher values in Soil-A than in Soil-B (Table 5). Considering all the background electrolyte solutions, adsorbed B content was higher in Soil-A than in Soil-B. According to the results (Table 5) and by using ANOVA one-way test, B adsorbed showed significant differences associated to the shaking time factor in all the treatments when using background electrolytes solutions, which was opposite to the result found in TBo for both soils. In Soil-A, the highest significant difference was recorded in TBK, however in Soil-B it was associated to TBMg and TBNa. According to ANOVA two-way test, background electrolytes and shaking time gave statistical significant differences in both soils. Moreover, ANOVA one-way test indicated that the background electrolyte composition of soil solution showed higher significant difference compared to shaking time. The B adsorbed by soils showed higher values in Soil-A than in Soil-B. This behavior was the same for the divalent cations $CaCl_2$ and $MgCl_2$ as background electrolytes. Considering NaCl and KCl, as it happened in the background electrolyte experiments with divalent cations, B adsorbed showed greater values in Soil-A than in Soil-B. For boric acid solution without a background electrolyte, the B adsorbed showed close values and it was independent of the time of shaking, and the B adsorption probably reached the maximum within the first h of shaking. The ANOVA test confirmed no effect of shaking time. Fine textured soils can adsorb more B than coarse-textured soils due to the higher content of clay minerals (Al-Ameri *et al.,* 2019). Furthermore, the primary B adsorbing surfaces in soils are the surface area of soil clay minerals, calcium carbonate, aluminum and iron oxides, and organic matter (Goldberg, 1997; Al-Ameri *et al.,* 2019). In the present study, the significant differences found by using T test ($P<0.05$) indicated that 1 h of shaking is not the sufficient time needed to reach B saturation on adsorption sites. Consequently, in both soils, 3 h appeared to be enough time in which the soil reaches maximum B adsorption. Boron adsorption showed significant differences (Table 5) considering the shaking time in all the treatments when using background electrolytes solutions. On the other hand, no significant differences were found in TBo for both soils. This result reinforces the importance of the shaking time and 3 h of shaking to reach the maximum adsorption value in the presence of background electrolyte for the determination of B adsorption in soils. However, this result is not in line with Hingston's findings (1964). He studied the effect of shaking time on B adsorption by Willalooka illite in 0.01 M $CaCl_2$. He found that adsorbed amounts of B were similar at shaking times from 30 min to 2 days. Moreover, it should be noted that even after several weeks, there was no significant difference observed. This indicates that soil is a complex system, and it is important to the texture and the presence of other ions interacting with the soil solution, among other properties commented previously. Using ANOVA two-way test, background electrolytes and shaking time gave significant differences for both soils (Soil-A and Soil-B). In addition, the background electrolyte composition of soil solution was obviously the factor of higher interest compared to shaking time, as previously indicated by ANOVA one-way test indicated. B adsorption is dependent on the soil texture (Al-Ameri *et al.,* 2019). In this case, the clay loam texture of Soil-A retained more B than the sandy loam texture of Soil-B. Actually, fine-textured soils can adsorb more B than coarse-textured soils due to their clay minerals content (high specific surface and cation exchange capacity) (Al-Ameri *et al.,* 2019). The presence of the clay minerals like montmorillonite and chlorite especially enhance B adsorption (Goldberg, 1997; Al-Ameri *et al.,* 2019). This finding was also confirmed by many other research investigations. According to Gürel *et al.* (2019) adsorbed B level heightened with an increase in clay content. Moreover, B deficiency has been commonly reported in coarse-textured acid soils of humid regions (Alam and Jahan, 2007). Although B adsorption could be associated to the presence of soil organic matter, as organic matter also contributes to B adsorption, the influence of fine texture may be the most important factor in soils with low organic matter content. Essential soil properties such as clay and organic matter content have been constantly mentioned to influence B distribution in soil (Irfan *et al.,* 2019).Organic matter content in the two soils is considered as low (Table 3). According to López *et al.* (2017), soil organic carbon levels are generally low or very low in the Mediterranean region of eastern Morocco, northern Algeria, Tunisia and western Libya. According to Sarkar *et al.* (2014), the low organic matter content in the soil resulted in an increase of B adsorption, as the sites of adsorption of oxides and hydroxides of Fe and Al on mineral surfaces are activated. Furthermore, at the same equilibrium concentration, the frequency of these processes is greater in clayey soils than in sandy loam soils (Rodrigues and Silva, 2020). This could explain the fact that soil-A adsorbs more B than soil-B.

Background electrolytes influence on B adsorption

Following the comparison of all the mean values of B adsorbed in all types of background electrolytes solutions, in both soil-A and B, minor B adsorption was found using boric acid solution without background electrolytes (Figs. 3 and 4). This proves that cations presented in background electrolyte solutions are having an important role in B adsorption. In Soil-A, the highest adsorbed B mean value was found with K, monovalent cation, although so close to the rest of the mean values excepting TBo and in Soil-B was associated to Ca, divalent cation. Focusing on $CaCl_2$ and NaCl, as a comparison of divalent and monovalent cations, the content of B adsorbed was higher with the solution containing $CaCl_2$ than in the NaCl solution, as reported earlier by Goldberg and Suárez (2011). They explained that in the Ca, the slightly greater B adsorption at high pH was caused by B adsorption onto freshly precipitated $CaCO_3$. Goldberg and Forster (1991), Goldberg (1997) and Kumar *et al.* (2018) highlighted that, in calcareous soils, calcium carbonate is an important B adsorbing surface. This confirms very well the finding of this work, as the two soils of this case study are calcareous (rich in limestone). Furthermore, ionic strength has a significant effect on B adsorption, being more important in the presence of a divalent ion such as calcium than monovalent sodium ions

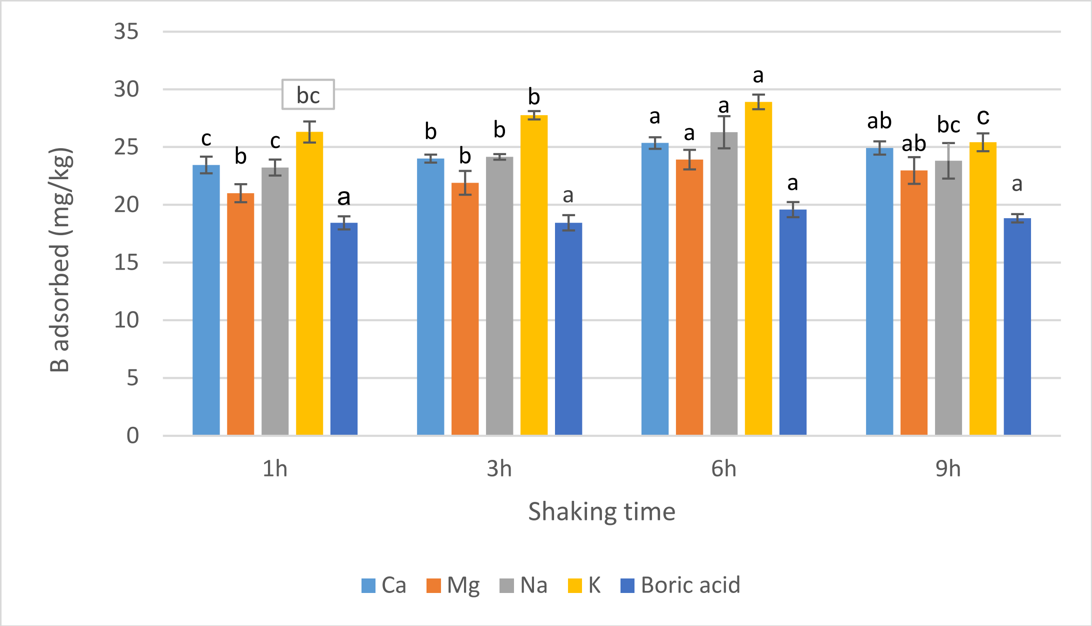

Fig.3: B adsorbed in Soil-A with different time of shaking in TBCa, TBMg, TBNa, TBK and TBo (Different letters indicate significant differences among the different time of shaking at P<0.05 level and at the same treatment)

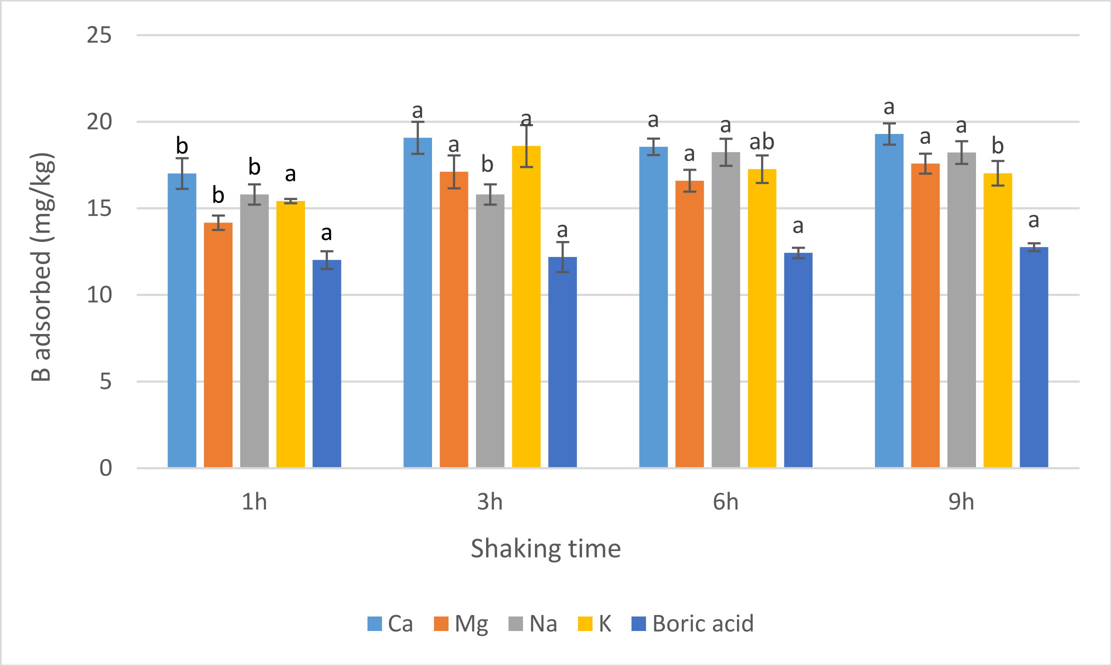

Fig.4: B adsorbed in Soil-B with different time of shaking in TBCa, TBMg, TBNa, TBK and TBo (Different letters indicate significant differences among the different time of shaking at P<0.05 level and at the same treatment)

(Rodrigues and Silva, 2020). As for clay minerals, Keren and Sparks (1994) have concluded that the negative electrical field associated with the planar surface affects the B adsorption on edge surfaces. They explained that for clay minerals, increasing ionic strength eliminates the negative electrical field of planar surface. As a result, more negative borate ions are able to approach the adsorption sites on the edge surfaces and interact with them, which contributes to greater B adsorption. Moreover, Abu-Sharar *et al.* (2014) confirmed Majidi *et al.* (2010) finding that an increasing background electrolyte concentration 0.01 M NaCl to 0.1 and 0.5 M resulted in an elevation of the maximum of B adsorption by respectively 30% and 75%. Calcium chloride at the equimolar concentration showed a more important increase in B adsorption as compared to NaCl. A divalent system will have a higher ionic strength (I) than equimolar monovalent system causing more compressed diffused double layer. These findings prove the strong effect of Ca divalent cation in B adsorption. These authors further pointed out that B was mainly adsorbed as an outer-sphere complex, favored by the presence of micro-aggregates; clay particles attached to organic molecules by polyvalent cations (Bronick and Lal, 2005). In short experiments, studying the effect of KCl on boric acid solutions, no decrease in the B concentration was found, even at higher K concentrations than in soil solution. This means that the potassium did not have a direct effect on B adsorption, but created new conditions in the soil, which favor B adsorption or provided new adsorption sites with high affinity for B (Hadas and Hagin, 1972; Tariq and Mott, 2007). This could explain somehow the results, that greater B adsorption was found in K monovalent cation in clay loam soil (Soil-A). However, no significant differences were found between K and Ca as background electrolytes. Ionic strength affects significantly B adsorption. This effect has been reported low for oxides and high for clay minerals and soils (Mattigod *et al.,* 1985; Majidi *et al.,* 2010). However, in the present study, in which Soil-B is sandy loam soil, B adsorbed highest value is associated with Ca background electrolyte solution. In clay loam soil, Soil-A (that obviously contains more clay than Soil-B), B highest adsorbed value is not associated to divalent cation as expected, but to K monovalent cation. Mattigod *et al.* (1985) and Kot (2009) developed that borate ions combine with alkali and alkaline earth cations to produce soluble complexes. Therefore, the formation of borate complexes in solution may influence the adsorption of this element on mineral surfaces. These authors highlighted the potential importance of ion-pair formation in K^+ and Ca^{2+} dominated electrolyte solutions in the context of B adsorption on kaolinite.

CONCLUSION

The Boron adsorption in soils is a significant topic in agronomy, as it can threaten plant development and crop yield. In this study, B adsorption was investigated in calcareous salt-affected soil in semiarid areas, under the effect of different background electrolytes, two soil textures and different shaking time intervals. The study findings revealed that Soil-A (clay loam) adsorbed more B than Soil-B (sandy loam), owing to soil texture and possibly organic matter content. It is of great relevance that soil texture and organic matter are key factors that can explain the boron adsorption in soils and both should be checked in cultivated soils to ensure the bioavailability of this plant nutrient. However, the analysis of boron to measure the presence and interactions with the soil matrix is a great concern. Beyond any doubt, the shaking time may have a significant impact on B adsorption in soils, as it takes 3 h of shaking to reach the maximum amount of B adsorbed. The results showed that the background electrolyte composition of soil solution is a factor of highest interest in boron adsorption mechanism. Centered in the current study, concerning Soil-A, the maximum B adsorption value was recorded with potassium chloride. As for Soil-B, it was associated with calcium chloride. Furthermore, the content of B adsorbed was higher with the solution containing calcium chloride than sodium chloride. In both soils, in general, the major B adsorption was reached by using calcium chloride as background electrolyte solution. Therefore, compared to all background electrolytes solutions, calcium chloride seemed to be the cation having the most favorable behavior for B adsorption experiments. In this sense, the presence of a predominant monovalent or divalent cation as a background electrolyte obviously determine the adsorption of B in soil and the availability of this nutrient to plants. In conclusion, the optimal conditions for maximum boron adsorption in this type of soils are characterized by calcium chloride background electrolyte in a determined shaking time interval equal to (3h) according to the present study. Consequently the high boron adsorbed results in a low rate of boron assimilation by plants, which decrease crop yields, agricultural productivity, and equally has a negative influence on the Tunisian national economy.

AUTHOR CONTRIBUTIONS

S. Fatnassi performed the literature review, experimental design, analyzed and interpreted the data, prepared the manuscript text, and manuscript edition. J. Navarro Pedreño performed the experiment supervision in Spain, literature review, compiled and interpreted the data and contributed to the draft manuscript preparation. M.B. Almendro Candel supported the experiment in the study laboratory of Agrochemistry and Environment department in Miguel Hernández University of Elche (UMH), data preparation and review of the manuscript. I. Gómez Lucas supported the entire work in the research laboratory in UMH and afforded the necessary material and chemical products. M. Hachicha supervised and supported the study, helped in the literature review and manuscript preparation and review.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest regarding the publication of this work. In addition, the ethical issues including plagiarism, informed consent, misconduct, data fabrication and, or falsification, double publication and, or submission, and redundancy have been completely witnessed by the authors.

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PUBLISHER'S NOTE

ABBREVIATIONS

%	Percent
Al	Aluminum
ANOVA	Analysis of variance
B	Boron
Ca	Calcium
CaCl2	Calcium chloride
Cl	Chloride
dS/m	deciSiemens per metre
EC	Electrical conductivity of the soil
Ecw	Electrical conductivity of TWW
FAO	Food and Agriculture Organization of the United Nations
Fe	Iron
H	Hour/ hours
HCO3	bicarbonate
ISO	International Organization for Standardization
JECFA	Joint FAO/WH Expert Committee on Food Additives
K	Potassium
KCl	Potassium chloride

Max.	Maximum
Min.	Minimum
mg/L	Milligrams per liter
mm	millimeter
m	meter
Mg/kg	Milligrams per kilogram
meq/L	Milliequivalents per liter
Mg	Magnesium
MgCl2	Magnesium chloride
Na	Sodium
NaCl	Sodium chloride
NF	French standard
NT	Tunisian standard
N	Normality
NS	Not significant
OM	Organic matter
pH	potential of hydrogen
SD	Standard deviation
SO4	Sulfate
TCaCO3	Total equivalent calcium carbonate
TBo	Treatment of B solution without background electrolyte
TBCa	Treatment with calcium chloride background electrolyte
TBMg	Treatment with magnesium chloride background electrolyte
TBNa	Treatment with sodium chloride background electrolyte
TBK	Treatment with potassium chloride background electrolyte
TWW	Treated wastewater
WHO	World Health Organization
w/v	Weight/volume

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AUTHOR (S) BIOSKETCHES

Fatnassi, S., M.Sc., [1]Department of Geology, Faculty of Sciences of Tunis, University of Tunis El Manar, 2092 El Manar, Tunis, Tunisia. [2]National Institute of Rural Engineering, Waters and Forest, Carthage University, 2080 BP 10 Ariana, Tunisia.

- Email: *salmapro14@gmail.com*
- ORCID: 0000-0002-2017-1056
- Web of Science ResearcherID: NA
- Scopus Author ID: NA
- Homepage: NA

AlmendroCandel, M.B., Ph.D., Associate Professor, Department of Agrochemistry and Environment, Miguel Hernández University of Elche, Avd.de la Universidad SN, 03202 Elche, Alicante, Spain.

- Email: *mb.almendro@goumh.umh.es*
- ORCID: 0000-0003-3704-8078
- Web of Science ResearcherID: K-8319-2014
- ScopusAuthor ID:9332378700
- Homepage: www.umh.es/contenido/Estudios/:persona_35434/datos_en.html

Navarro Pedreño, J., Ph.D., Professor, Department of Agrochemistry and Environment, Miguel Hernández University of Elche, Avd.de la Universidad SN, 03202 Elche, Alicante, Spain.

- Email:*jonavar@umh.es*
- ORCID: 0000-0002-4765-2191
- Web of Science ResearcherID:A-7830-2010
- Scopus Author ID:6602116441
- Homepage: https://www.umh.es/contenido/Estudios/:persona_5343/datos_en.html

Gómez Lucas, I., Ph.D., Professor, Department of Agrochemistry and Environment, Miguel Hernández University of Elche, Avd.de la Universidad SN, 03202 Elche, Alicante, Spain.

- Email: *ignacio.gomez@umh.es*
- ORCID: 0000-0002-0931-9654
- Web of Science ResearcherID: H-8531-2015
- Scopus Author ID: 16315845200
- Homepage: https://www.umh.es/contenido/Universidad/:persona_117889/datos_en.html

Hachicha, M.,Ph.D., Professor, National Institute of Rural Engineering, Waters and Forest, Carthage University, 2080 BP 10 Ariana, Tunisia.

- Email: *hachicha.mohamed@iresa.agrinet.tn*
- ORCID: 000-002-5125-8541
- Web of Science ResearcherID: NA
- Scopus Author ID: NA
- Homepage: http://www.lrvenc.agrinet.tn/cv/Medhcicha.html

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