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RESEARCH PAPER

How management practices affect silicon uptake by *Hordeum vulgare* grown in a highly calcareous soil

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Abstract

There are many studies on the beneficial effects of silicon (Si) in plants related to a decrease of stress (biotic/abiotic). The objective of the present work was to study how plant-available Si in highly calcareous soil with different soil chemical properties, amendments and growing conditions can affect Si absorption by *Hordeum vulgare* L. (Barley) and its biomass. Barley was cultivated under field conditions in dryland agriculture. Three treatments were compared: phytolithic biochar, compost pellets and no amendment. Greenhouse trials with the same soil and treatments were also carried out to achieve a better understanding of the dynamics in the soil–plant system under controlled growing conditions. In both experiments, physical and chemical soil and plant parameters were determined from collected samples. Results showed that the Si uptake and biomass in soils with the highest available Si (33 ± 1 mg kg^{-1}) was 4.7-fold and 2.4-fold higher, respectively, than in soils with the lowest available Si (22 ± 1 mg kg^{-1}). Also, with greater Si uptake there was an increase in N uptake ($\tau = 0.68$, $p < 0.01$). Therefore, Si could improve N use efficiency within the plant. A strategy to improve Si values would be to use organic amendments that are enriched with Si and supply N in a form other than ammonium (NH_4^+). A high pH in this type of soil produces dissolution of the biogenic Si pool and low electrical conductivity values improve plant-available Si values. It is important to increase plant-available Si in highly calcareous soils as this has important implications for improving barley production.

KEYWORDS

barley, biochar, compost pellet, highly calcareous soil, Si availability, soil properties

1 | INTRODUCTION

Silicon (Si) is the second most abundant element in soil, is mainly found in biogeochemical inert forms and is also a major inorganic constituent in higher plants. All plants grown in soil contain some Si in their tissues (Epstein, 2009) although the available Si in soil is low due to the degradation resistance of Si-containing minerals. Si is mainly absorbed by the plant roots as orthosilicic acid (H_4SiO_4) which is present in the soil solution where the most immediate source is adsorbed Si on the surfaces of inorganic, organic and organic–inorganic colloids in soil (Ma & Takahashi, 2002; Marschner, 2012). Therefore, its absorption by plants depends on the ability of the soil to provide Si. There are many studies that show beneficial effects of Si on plants (Epstein, 1994; Marschner, 2012). Moreover, there are studies on its behaviour in soils, mainly in paddy field soils (with a pH < 7) because of the economic importance of rice (Tsujimoto et al., 2014). But there are few publications on studying the Si behaviour in highly calcareous soils (Argeaa et al., 2016) which are common in arid and semiarid Mediterranean regions and which have high values of calcium carbonate ($CaCO_3$) (>25%) according to the classification given by FAO (2006), where important staple crops such as *Hordeum vulgare* L. (barley) are grown. Gattullo et al. (2016) studied Si dynamics in the rhizosphere of barley plants and their connections with iron mobilization in highly calcareous soils. Furthermore, Gunes et al. (2007) studied Si-mediated changes on some physiological and enzymatic parameters symptomatic of oxidative stress in barley plants grown in sodic toxic soil under highly calcareous conditions. Both studies were performed under controlled conditions.

Barley is one of the most important cereal crops cultivated and ranks within the top ten crops in the world. Spain is the seventh largest producer in the world of barley (FAO, 2014), and the regions of Castilla y León and Castilla-La Mancha are the largest producers within Spain. The latter region has large areas of highly calcareous soils where barley is often grown and has been affected by an increase in drought and higher temperatures over the last decades which in turn affects agricultural production (Gómez Cantero et al., 2018). According to the European Environment Agency, a reduction in crop yield for the period 2021–2050 is expected in southern Europe (EEA, 2019).

Calcareous soils cover more than 30% of the Earth's land surface and their $CaCO_3$ content ranges from a few per cent to 95% (Marschner, 2012) which influences their physicochemical characteristics. Management practices in calcareous soils differ from those in non-calcareous soils, because of the effect of soil pH and $CaCO_3$ content on properties related to plant growth and due to chemical reactions that affect the loss or fixation of almost all nutrients (FAO, 1973; Marschner, 2012). The magnitude of this effect varies according to the content of $CaCO_3$ and is greatest in highly calcareous soils where crop production is severely limited due to elevated $CaCO_3$ content that lowers nutrient availability (i.e., nitrogen [N] and phosphorous [P]), scarcity of available water, low organic matter (OM) content and formation of soil crusts (Wahba et al., 2019). In addition to these constraints, calcareous soil is poor in plant-available Si. The concentration of H_4SiO_4 is strongly dependent on the soil pH. At a soil pH of 8 to 9, it has the lowest concentration and below or above this range the concentration increases significantly (Liang et al., 2015). Meunier et al. (2018) suggested that pH values up to 7.5 can be used as a proxy for plant available Si. Therefore, barley grown in highly calcareous soils suffers from reduced nutrient availability and low OM content as well as drought stress. This will result in a lower yield than that obtained for more fertile soils. Si has far-reaching benefits for plants and could reduce abiotic stress, which improves barley production (Etesami & Jeong, 2020; Ma & Yamaji, 2006). The study of Si nutrition becomes important when the plants are under stressful conditions, whereas under favourable conditions its role is often minimal (Epstein, 2009).

It is known that continuous cropping removes large quantities of Si from soil in the range of 40–300 kg Si ha^{-1} for a wide range of crops (Matichenkov & Bocharnikova, 1994). Higher removal rates are expected from Si-accumulator crops such as cereals. For instance in the case of barley in the USA, the average Si removal rate is 125 kg ha^{-1} (Tubana et al., 2016). Applying soil amendments could provide a source of available Si to a soil and be absorbed by the corresponding crop cultivation.. Li et al. (2018) reported that phytolith-rich biochar could serve as a slow release source of available Si for plant in agricultural soils (highly weathered and desilicated); Li and Delvaux (2019) and Li et al. (2020) also reported that phytolithic biochar largely enhanced the biological Si feedback loop by increasing plant available Si. As a further alternative, García-Mendívil et al. (2014) reported that Si-enriched mushroom compost increased the average wheat yield. Therefore, improving the knowledge about how to sustainably increase plant-available Si in highly calcareous soil could improve the yield of barley.

The work hypothesis was that a greater available Si in highly calcareous soil would lead to an increased Si uptake by barley plants and as a consequence a greater biomass. The objectives in this work were to study: (i) how different soil chemical properties such as OM, pH, electrical conductivity (EC), N and treatments (with and without amendments) applied affected the available Si in highly calcareous soil under field conditions; (ii) how irrigation under controlled conditions affected Si, N and P absorption by barley plants; and (iii) how available Si in this soil type affected Si absorption by barley plants and the resulting biomass.

2 | MATERIALS AND METHODS

2.1 | Field experiment

The study site is located in Buendía (40°22′10″N/2°46′19″W) within the Autonomous region of Castilla-La Mancha in Central Spain at an altitude of 732 m above sea level. The region is under the influence of a Continental Mediterranean climate with dry and hot summer conditions, quite cold winters and sparse precipitation (Table 1). The site is on marginal land with soil containing a high carbonate and low OM contents, an abundance of stone fraction and where high pH values limit essential nutrient uptake.

The field experiment was carried out during the winter through to the summer period of January to June 2017, respectively. In this period the total precipitation of 190 mm (Table 1) was well below the average corresponding to a period of 30 years for the region (264 mm; AEMET, 2021) indicating drought conditions. Two-row barley (*Hordeum* *vulgare* L. var. Pewter) cereal was cultivated in dryland agriculture. Three treatments were compared: 0.5% of phytolithic biochar (applied at a rate of 10 t ha^{-1}), 3.8 t ha^{-1} of compost pellets and no amendment. The amount of biochar applied was according to the recommendations given by the Joint Research Center (Verheijen et al., 2010). In the case of compost pellets, the application rate was based on the nutritional requirement (N, P and potassium [K]) of barley. The study site was 396 m^2 and was divided into square plots of 4 m^2 (Figure 1). Six plots were selected at random for each treatment.

The phytolithic biochar came from local woody remains obtained from the immediate surroundings (pruning from olive 30% and pine 70%). The feedstock was dried to approximately 15% moisture (w/w) and was pyrolysed at 750ºC. The pellets originated from compost of spent mushroom substrate, bio-residues from biogas production and poultry manure. Biochar was introduced to the soil three months before sowing the barley to facilitate appropriate soil incorporation and pellets were applied at the same time the soil was seeded.

Soil sampling (ISO 10381–2, 2002) was performed following the probability sampling protocol. Random soil

TABLE 1 Meteorological conditions in the cultivation year (AEMET, 2017)

Temperature (ºC)				Precipitation (mm)		
T-min	T-max	T-lowest	T-highest	P-tot acc	P-max	P-average
9.1	22.4	−5.4	39.4	190	27.8	0.7

T-min, average minimum temperature; T-max, average maximum temperature; T-lowest, the lowest recorded temperature; T-highest, the highest recorded temperature; P-tot acc, total accumulated precipitation; P-max: average maximum precipitation.

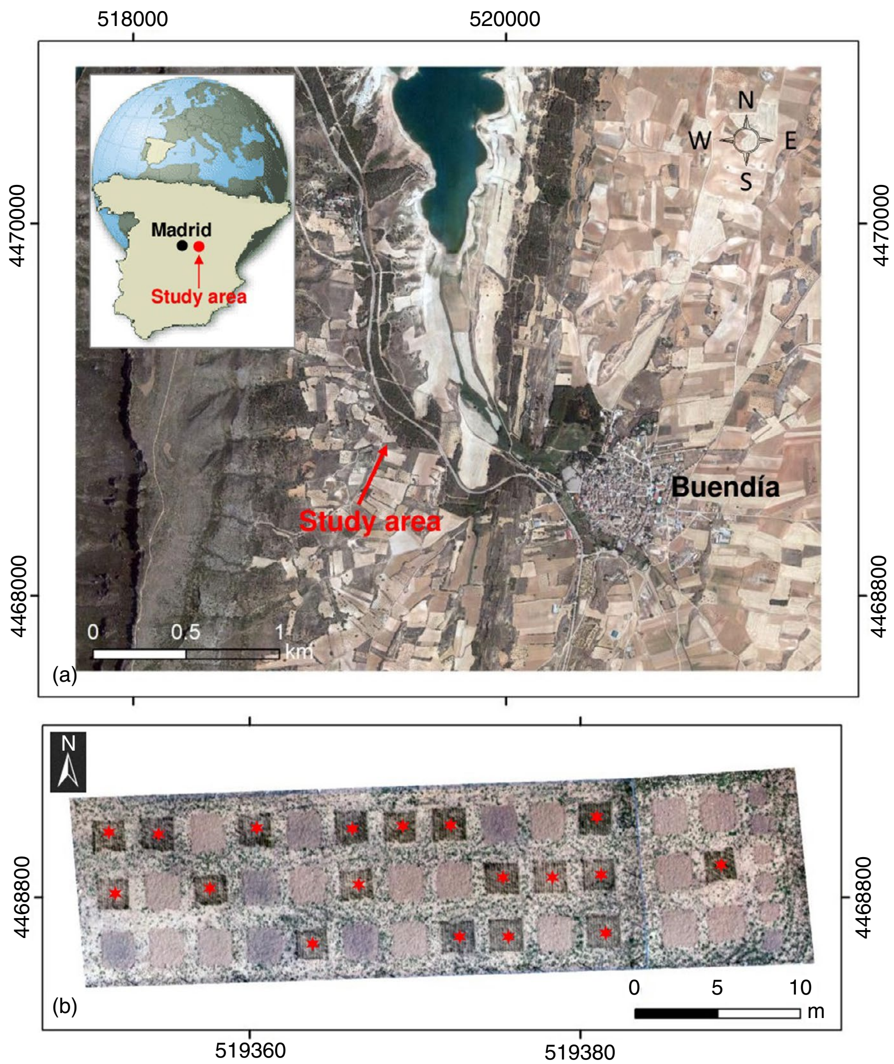

FIGURE 1 Location of the test site (a) near the town of Buendía in the Province of Cuenca, autonomous community of Castilla-La Mancha and (b) the field plots of barley used in the work (marked with a red asterisk)

samples were taken within a systematic square grid area in each plot (Huesemann, 1994). The grid was divided into nine blocks, and these in turn were further divided into nine sub-blocks with numbers assigned (1–9). Nine soil sub-samples were taken to make a composite sample for chemical laboratory analysis. The sub-samples were taken according to the block and sub-block selected by generating random numbers in a Microsoft Excel worksheet. All sample depths were 0–20 cm of the topsoil layer. The samples were collected before sowing and after harvesting the rainfed barley plants. Plant sampling was performed using a quadrat of 1 m^2 in the middle of every plot. The above-ground (plant) biomass was sampled at plant maturity. The weights of whole biomass and grains and the number of ears were counted.

2.2 | Experimental work under greenhouse conditions

The role of Si in the soil–plant system was assessed in barley by controlled irrigation in a greenhouse trial to simulate optimal conditions for cultivation. This experimental set-up was therefore used to the study the irrigation effect on the chemical characteristics of the soil and, consequently, on the absorption of Si, N and P by the barley plant.

Barley plants were grown in pots (16 cm diameter × 15[h] cm) filled with 2 kg of soil from the study area where the experimental field work was carried out. The crop density was six plants per pot the same sowing density used in the field study area. The same experiment treatments that were applied to the field site were used in the pot experiments as follows: biochar (15-pots), pellets (15-pots) and without any amendment (nine pots). Each pot per treatment represented one replication.

Greenhouse environmental conditions were maintained as follows: (1) night and day average temperatures of 12 and 26ºC, respectively; and (2) a relative humidity of 45%–70%. Watering was carried out according to crop requirements by drip irrigation to avoid plant drought stress.

Soil samples were collected from each pot before sowing and after harvesting. In this case, two soil sub-samples was taken to have a composite sample for the chemical laboratory analysis. All above-ground (plant) biomass was sampled at maturity in each pot.

2.3 | Soil and plant analysis

The soil samples were air-dried and sieved to a fine fraction (<2 mm). Thereafter, different soil properties were measured which included pH (soil/water-1:2.5); EC (soil/water-1:5); OM multiplying by 1.724 the oxidizable organic carbon which was determined by wet acid oxidation and applying a recovery factor = 1 (Walkley, 1947; Walkley & Black, 1934); soluble ammonium (NH_4^+), NO_3^-, Ca^{2+} and SO_4^{2-} (ion chromatography); and plant-available P (Burriel & Hernando, 1950). Furthermore, one part of the soil fine fraction was ground in an agate mortar (RM 200; Retsch) to analyse N-Kjeldhal that was determined by concentrated sulphuric acid digestion (Digestion Unit Büchi K-435) and steam distillation (Scrubber Büchi B-414 and Distillation Unit Büchi K-360) to finally determine reduced nitrogen forms by a boric acid titration (Titriator Metrohm 848 Titrino plus).

The plant samples were oven-dried at 105ºC for 2 h, thereafter, placed into a desiccator and then ground to powder in an agate mortar (RM 200; Retsch). Plant analyses included N (N-Kjeldhal) and P (microwave digestion: nitric acid and hydrogen peroxide/combined reagent: sulphuric acid+antimony potassium tartrate+ammonium molybdate+ascorbic acid/spectrophotometry at 880 nm).

2.4 | Extraction and determination of Si in soil and plant samples

Si was extracted from the plant samples in the form of silicon dioxide ($SiO_2.nH_2O$) and converted into H_4SiO_4 by digestion with hydrogen peroxide (H_2O_2) under alkaline conditions using sodium hydroxide (NaOH-50%). This analytical method was modified specifically for cereal material according to the method described by Estefan et al. (2013) based on Korndörfer et al. (2004).

Plant-available Si in soil was extracted with $CaCl_2$ (0.01 M). This analytical method was carried out and modified according to the method described by Estefan et al. (2013) based on Korndörfer et al. (1999) and Haysom and Chapman (1975).

In both cases, Si was determined colorimetrically by reaction with molybdate according to method 370.1 (EPA-600/4–79–020, 1983) adapted to our sample material. The absorbance by spectrophotometer (Thermo Scientific Evolution 300 UV-Vis) was read at 810 nm.

Certified reference material BCR-060 (aquatic plant, 2.85%), NCS DC 73348 (bush branches and leaves, 0.58% ± 0.04%) and standard addition (Si standard solution, Si = 1 g l^{-1} for AAS, PanReac AppliChem) were used for the internal control of the methods. The relative deviation standard for repeatability was ≤15%, and the relative uncertainty associated with the method (k = 2) was ±20%.

2.5 | Statistical analysis

The software package used to perform the statistical analysis was SPSS for Windows (version 14.0, IBM). The Student

t-test was used to compare the means of the following data sets: (1) different soil properties with different treatments and (2) Si, N and P in barley with different treatments. The significance level was $\alpha = 0.01$.

Kendall's tau-b correlation test was applied to: (1) Si extracted by $CaCl_2$ and straw Si; (2) straw Si and plant biomass; (3) straw Si, straw N and straw P; and (4) Si uptake, N uptake, grain weight of barley and number of ears. The correlation was significant at the level 0.01 and 0.05 depending on the case.

Furthermore, the PLS package of R statistical environment (version 2.6-0, Mevik & Wehrens, 2007) was used to perform a Principal Component Regression (PCR) analysis. The PCR analysis was chosen in order to avoid collinearity between the different variables, and it was used to determine how different soil chemical properties influence the Si accumulation in barley (maturity).

3 | RESULTS

3.1 | Soil and amendments

Soil parameters measured before sowing indicate that the studied soil had a low OM content, moderately alkaline pH, high $CaCO_3$ content (52% ± 3%), sandy clay loam, loam and clay loam textures (clay: 26% ± 1.9%, silt: 28% ± 3.6%, sand: 47% ± 3.4%), medium values of total N, low to medium values of available P and low EC that would be suitable for crop production (Tables 2 and 3). The values of plant-available Si

TABLE 2 Chemical characterization of soil under rainfed field conditions at the beginning of the experiment and after harvesting considering the different treatments

	Before sowing	After harvesting		
Chemical parameter	**Original soil**	**No treatment**	**Biochar**	**Pellet**
pH	8.4 ± 0.02	8.2 ± 0.03a	8.3 ± 0.03a	8.3 ± 0.04a
EC (µS cm^{-1})	149 ± 6	194 ± 14a	176 ± 8a	198 ± 10a
OM (%)	1.22 ± 0.02	1.20 ± 0.04a	1.19 ± 0.05a	1.18 ± 0.04a
N (%)	0.17 ± 0.003	0.14 ± 0.03a	0.16 ± 0.01a	0.16 ± 0.01a
NO_3^- (mg kg^{-1})	140 ± 7	144 ± 19a	110 ± 7a	124 ± 13a
NH_4^+ (mg kg^{-1})	21.3 ± 4.8	0a	0a	0a
Available P (mg kg^{-1})	12.5 ± 0.6	12.7 ± 2.6a	9.5 ± 0.6a	9.8 ± 1.2a
Ca^{2+} (mg kg^{-1})	680 ± 14	837 ± 46a	869 ± 27a	913 ± 23a
SO_4^{2+} (mg kg^{-1})	56 ± 3	156 ± 16a	161 ± 11a	192 ± 19a
Si extracted by $CaCl_2$ (mg kg^{-1})	33 ± 1	29 ± 1a	30 ± 1a	30 ± 1a

The values after harvesting (mean ± *SE*) followed by the same letter (within the same chemical parameter) do not differ significantly at $p < 0.01$ with the Student t-test.

TABLE 3 Chemical characterization of soil under greenhouse conditions (irrigated) at the beginning of the experiment and after harvesting considering the different treatments

	Before sowing	After harvesting		
Chemical parameters	**Original soil**	**No treatment**	**Biochar**	**Pellet**
pH	8.4 ± 0.01	8.1 ± 0.03a	8.1 ± 0.03a	8.0 ± 0.02a
EC (µS cm^{-1})	188 ± 1	253 ± 13a	307 ± 19ab	333 ± 21b
OM (%)	1.14 ± 0.04	0.89 ± 0.02a	0.96 ± 0.02a	1.09 ± 0.01b
N (%)	0.18 ± 0.001	0.16 ± 0.01a	0.16 ± 0.01a	0.17 ± 0.002a
NO_3^- (mg kg^{-1})	96 ± 3	125 ± 8a	209 ± 14b	188 ± 15b
NH_4^+ (mg kg^{-1})	9.8 ± 0.6	0.5 ± 0.5a	0a	0.3 ± 0.2a
Available P (mg kg^{-1})	13.3 ± 0.5	8.4 ± 0.3a	8.7 ± 0.5a	9.2 ± 0.5a
Ca^{2+} (mg kg^{-1})	948 ± 7	963 ± 25a	1061 ± 43ab	1145 ± 46b
SO_4^{2+} (mg kg^{-1})	31 ± 5	91 ± 16a	193 ± 16b	297 ± 48b
Si extracted by $CaCl_2$ (mg kg^{-1})	23 ± 0.3	25 ± 1a	22 ± 1b	25 ± 1a

The values after harvesting (mean ± *SE*) followed by the same letter (within the same chemical parameter) do not differ significantly at $p < 0.01$ with the Student t-test.

ranged from 21 to 37 mg kg^{-1}. In this case, the soil parameters showed that this marginal land has a limited capacity for agricultural use.

The chemical characterization of compost pellets and phytolithic biochar is shown in Table 4. The pH of biochar was almost 2 units higher than the pH of the original soil whereas the pH of pellets was almost 1 unit lower. However, these differences were not significant because of the buffer capacity of the calcareous soil. Moreover, EC, OM, N, available P and sulphates (SO_4^{2+}) of biochar and pellets were higher than the values in the original soil and therefore the additional content of these different parameters could result in potential changes to the original soil. The concentrations of nitrates (NO_3^-) and calcium (Ca^{2+}) of biochar were similar to the values of the original soil, while the values of these variables in the case of pellets were much higher. Finally, the Si extracted by calcium chloride ($CaCl_2$) in the case of biochar was between 2 and 3 times lower than the Si in the original soil. In contrast, the Si extracted in pellets was similar to the Si in the original soil.

After one agricultural cycle and once barley was harvested, there were changes observed in the soil properties values (Tables 2 and 3). The values of pH and NH_4^+ significantly decreased ($p < 0.01$), while EC, Ca^{2+} and SO_4^{2+} significantly increased ($p < 0.01$) both in the soil under field conditions and in the irrigated soil under greenhouse conditions. The OM, N-Kjeldahl and available P values remained stable in the soil under field conditions, whereas they significantly decreased ($p < 0.01$) in the irrigated soil. The opposite occurred with the NO_3^- values. Finally, soil Si extracted by $CaCl_2$ significantly decreased ($p < 0.01$) in the soil under field conditions, whereas the values remained stable in the irrigated soil.

In the case of soil under field conditions, if the applied amendments are separately considered there were no significant differences among treatments for any soil variable after one agricultural cycle (Table 2). However, in the case of the experiments performed under more favourable conditions with irrigation, there were significant differences ($p < 0.01$) among treatments for the soil Si extracted by $CaCl_2$, OM, NO_3^-, SO_4^-, Ca^{2+} and EC (Table 3). The extracted Si in soil from the plots where biochar amendment was applied was significantly lower ($p < 0.01$) than in the soil where pellets or no amendment were applied.

3.2 | Barley plant responses

The dynamics of Si, N and P absorption in the soil–plant system under field conditions for the different treatments (Figure 2) show no significant differences ($p > 0.01$). An exception was of N uptake from pellets which was significantly higher than from no treatment. Furthermore, the biomass in

TABLE 4 Chemical characterization of the applied biochar and pellets. Each value represents the average of three replicates ±*SE*

Amendment	pH	EC (µS cm^{-1})	OM (%)	N (%)	NO_3^- (mg kg^{-1})	NH_4^+ (mg kg^{-1})	Available P (mg kg^{-1})	Ca^{2+} (mg kg^{-1})	SO_4^{2+} (mg kg^{-1})	Si extracted by $CaCl_2$ (mg kg^{-1})
Biochar	10.1 ± 0.1	978 ± 55	6.5 ± 0.2	0.52 ± 0.03	100 ± 5	0	298 ± 41	928 ± 53	153 ± 10	10 ± 1
Pellets	7.5 ± 0.1	8450 ± 251	12.8 ± 0.2	1.78 ± 0.06	6051 ± 57	0	5381 ± 66	20425 ± 207	27774 ± 671	18 ± 2

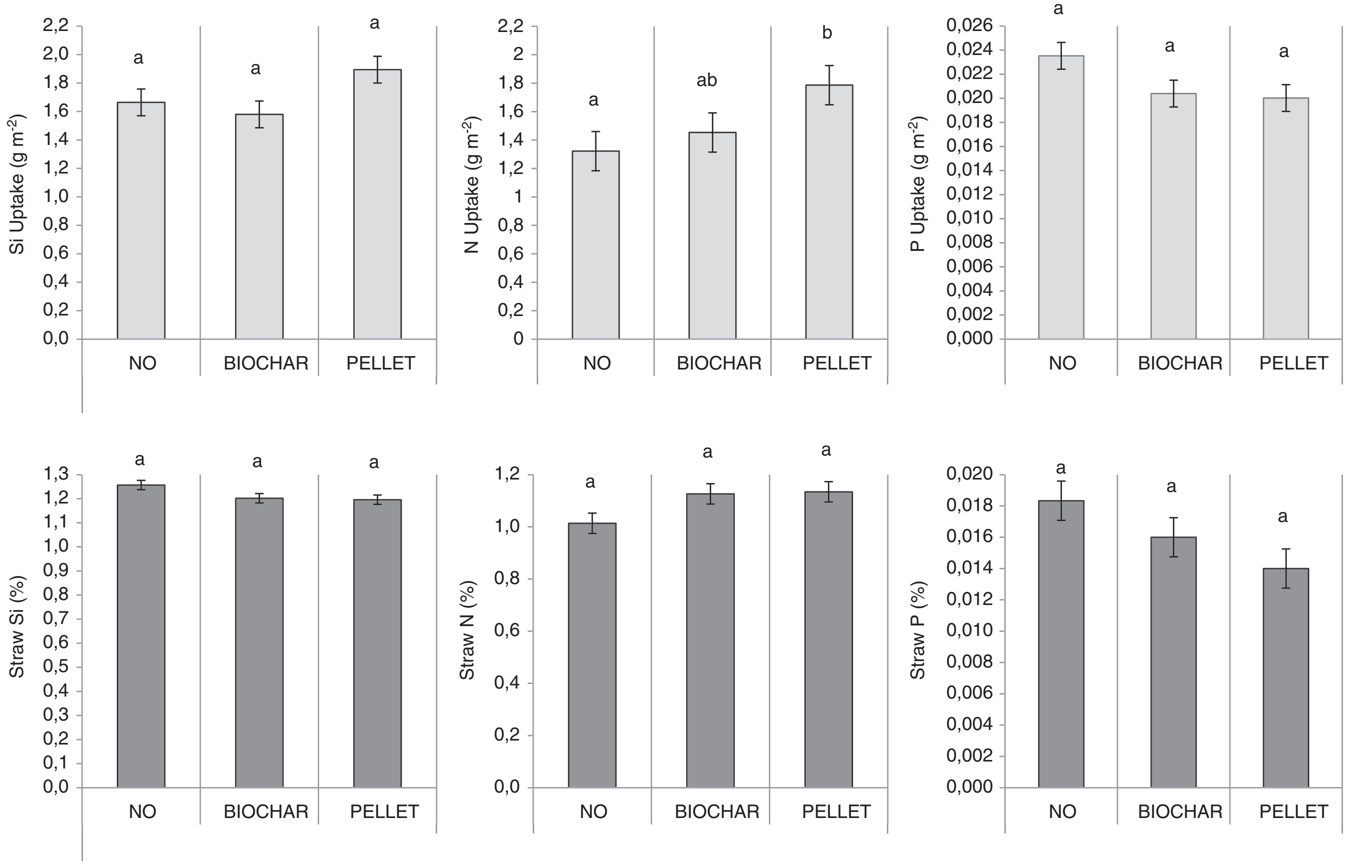

FIGURE 2 Straw Si, N and P concentration and Si, N and P uptake at maturity of rainfed barley grown in field site. The values are mean values ± *SE* ($n = 18$)

the soil with pellet amendment was 1.2-fold higher than the biomass in the soil without any treatment.

Under more favourable conditions for cultivation (greenhouse/irrigation), the dynamics of Si, N and P absorption in the soil–plant systems (Figure 3) again show no significant differences ($p > 0.01$). However, there was an exception of P uptake from pellets which was significantly higher than from biochar. This time the biomass in the soil with pellet was 1.2-fold higher than the biomass in the soil with biochar.

The trends of Si and N uptake under field conditions and greenhouse were similar. However, the trend of P uptake was different under field than under greenhouse. Under greenhouse conditions, it was higher from pellet than from the other treatments, while under field conditions, P uptake was higher from the soil without treatment than from the other treatments. Moreover, the magnitudes of concentrations and uptakes were different between field and greenhouse. The Si concentration of barley grown in rainfed soil under field conditions was twice as high as the Si in barley from greenhouse irrigated soil. However, the N and P concentration of barley grown in rainfed soil was 1.5-fold and 4-fold lower, respectively, than barley grown in greenhouse conditions. The Si uptake and N uptake in rainfed soil were 4.6-fold and 1.5-fold higher, respectively, than barley grown in greenhouse conditions. This coincided with the fact that the biomass in rainfed soil was 2.4-fold higher than barley grown in the irrigated soil. However, the P uptake in rainfed soil was 2-fold lower.

Considering rainfed and irrigated cases together, the plant biomass increased as the straw Si increased at maturity (Figure 4). Three separate trendlines for the different amendments with a high coefficient of determination (R^2) were determined.

Table 5 shows that the biomass, number of ears and grain weight of barley grown in the soil with pellets were higher than those in the other cases. This coincides with the highest Si and N uptake shown in Figure 2. The higher the Si uptake and N uptake, the higher the number of ears ($\tau = 0.68$, $p < 0.01$; $\tau = 0.42$, $p < 0.05$, respectively) and grain weight of barley ($\tau = 0.58$, $p < 0.01$, $\tau = 0.44$, $p < 0.05$, respectively).

3.3 | Soil–plant system

An increase in the Si concentration in barley with the increase in Si extracted by $CaCl_2$ considering all studied cases can be observed (Figure 5). Taking into account the different treatments, the correlation between soil Si extracted by $CaCl_2$ and

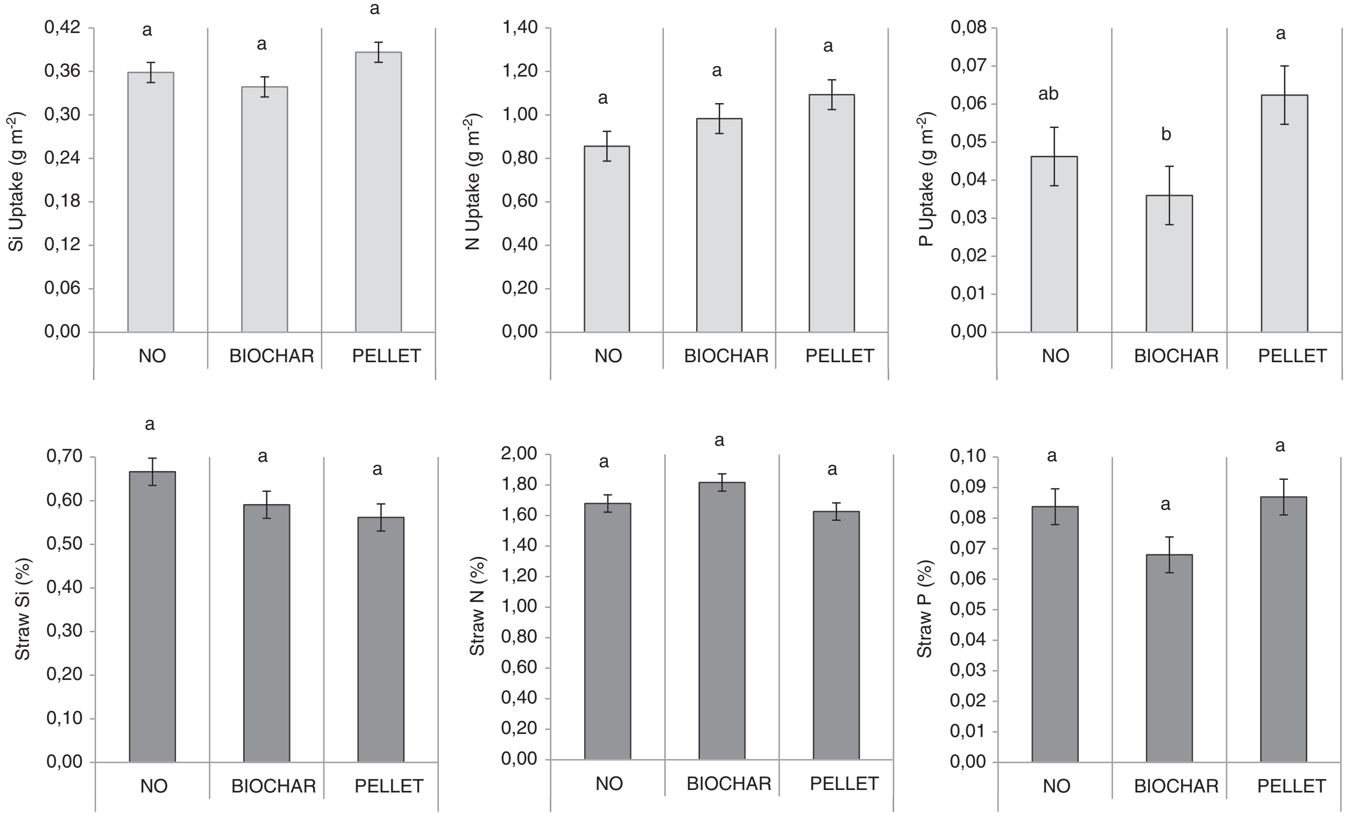

FIGURE 3 Straw Si, N and P concentration and Si, N and P uptake at maturity of barley grown under greenhouse conditions with irrigation (with soil from the test site). The values are mean values ± *SE* ($n = 39$)

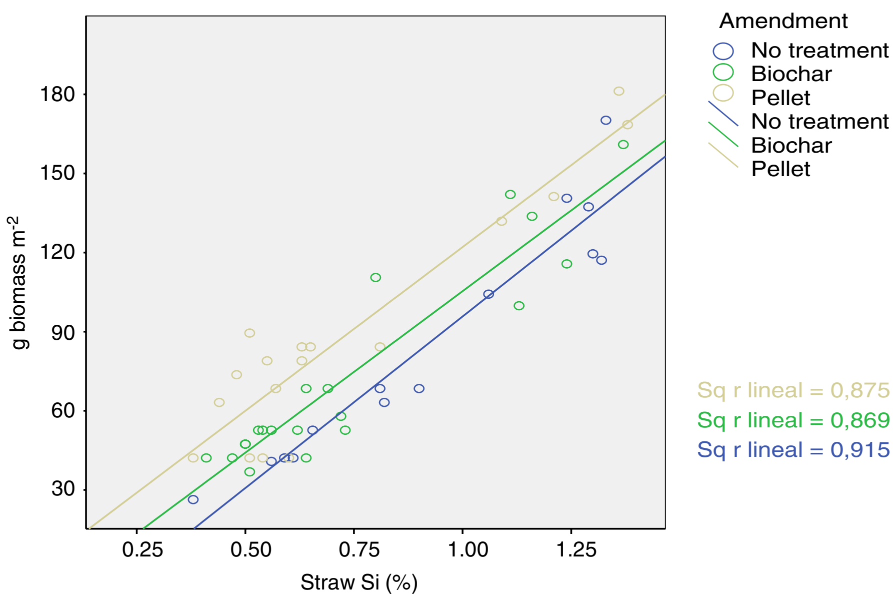

FIGURE 4 Relationship between the concentration of Si in barley straw and the biomass of the plant at maturity considering rainfed and irrigated cases together ($n = 57$)

barley Si was increased in the soil in which no amendment was applied and in which biochar was applied with respect to the case of all soil samples together (Table 6).

The statistical description of the cross-validated PCR model obtained for biochar and for pellet shows that values are similar in both cases (Table 7). The regression coefficients obtained for the two datasets (biochar and pellet) show how the individual soil properties influence Si accumulation in barley and as a consequence in the plant biomass (Figure 6). Accordingly, the most significant trends which were evident in all datasets were the high positive regression coefficients of the plant-available Si and the negative regression coefficients of the N-Kjeldahl. Another important trend is the positive relation of OM in the case of the

TABLE 5 Biomass, number of ears and grain weight of barley plants (mean ±standard error) for the different treatments (pellet, biochar and no treatment)

Treatment	Biomass ($g\ m^{-2}$)	Nº of ears	Grain weight ($g\ m^{-2}$)
Pellet	157 ± 18	312 ± 42	66 ± 13
Biochar	130 ± 21	264 ± 45	47 ± 16
No treatment	131 ± 21	250 ± 64	46 ± 19

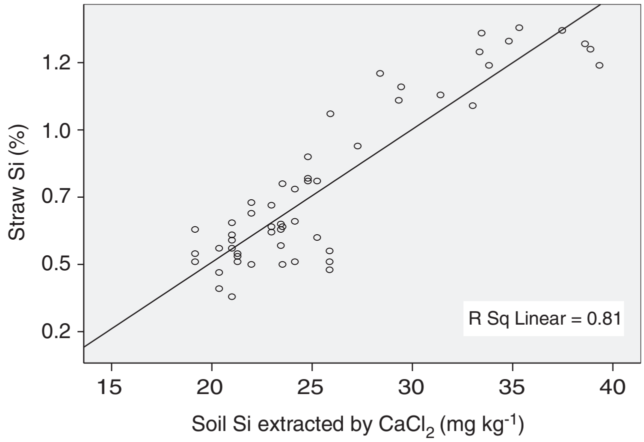

FIGURE 5 Relationship between the soil Si extracted by $CaCl_2$ and the Si concentration in barley straw at maturity ($n = 57$)

TABLE 6 Correlation coefficients between the Si extracted by $CaCl_2$ and the concentration of Si in barley straw grown in soils without amendment, in soils with biochar, in soils with pellets and in all soils by Kendall Tau-b test ($p < 0.01$ ** and $p < 0.05$ *) ($n = 57$: rainfed soils and irrigated soils)

	Concentration of Si in barley straw			
Tau-b correlation	Without amendment	With biochar	With pellets	All cases
Si extracted by $CaCl_2$	0.76**	0.68**	0.49*	0.61**

biochar dataset and the negative relation of Ca^{2+} and EC and the positive relation of pH in the case of the pellet dataset.

4 | DISCUSSION

4.1 | Soil

Changes of several soil properties were observed already after one agricultural cycle due to the different treatments with or without amendments that were applied and contrasting cultivation conditions. Under field conditions, the Si extracted by $CaCl_2$ significantly decreased ($p < 0.01$) compared with the original soil before barley sowing. However, under greenhouse conditions which were considered more favourable for cultivation, Si values in the soil were maintained although Si uptake by plants was 4.7 times lower than under field conditions. Water availability in the irrigated soil led to Si leaching although soil chemical equilibrium was kept. Moreover, the Si extracted by $CaCl_2$ was well correlated with the barley Si extracted by NaOH and H_2O_2 (Table 6, Figure 5) which shows that the soil Si extraction method is appropriate for obtaining available Si for barley grown in the present highly calcareous soil. Considering different groups classified according to the applied treatment (no amendment,

TABLE 7 Statistical description of the cross-validated PCR model obtained for the different amendments: biochar and pellet. Root mean square error of prediction (RMSEP), R^2 and p-value are the performance indices for the models evaluated

Amendment	RMSEP	R^2	p (>F)
Biochar	0.163	0.81	<0.001
Pellet	0.237	0.67	<0.001

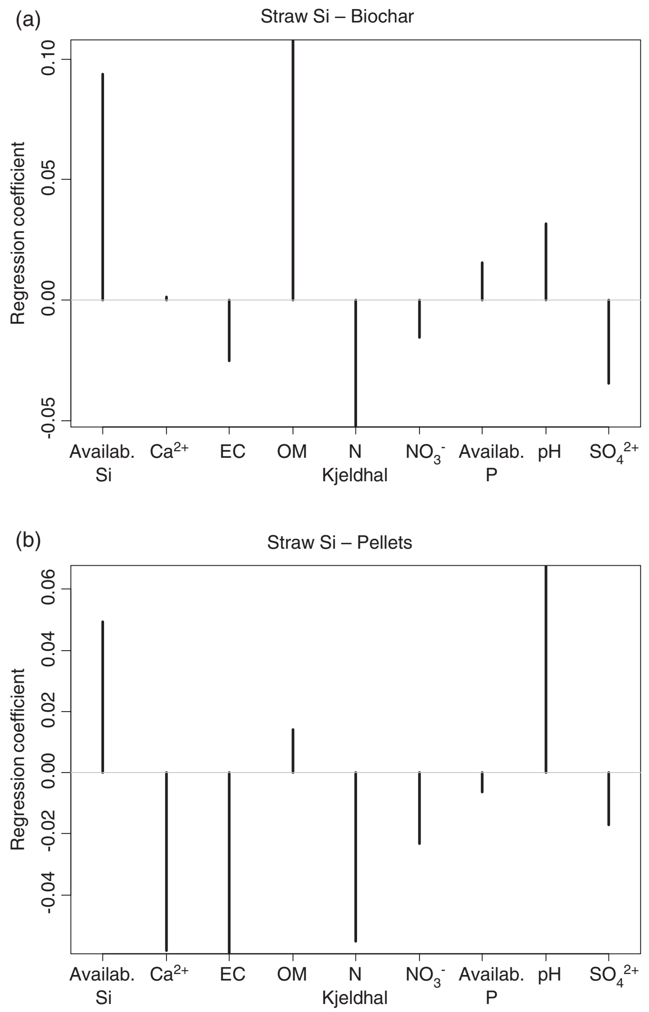

FIGURE 6 Regression coefficients of the PCR models using the soil parameters to describe the straw Si, (a) with biochar ($n = 21$) and (b) with pellets ($n = 21$)

biochar and pellet), significant correlation was still observed in each case (Table 6). Regarding the available Si values, they were similar or slightly higher than 20 mg kg^{-1}, which is the critical limit for soil Si extracted by 0.01 M $CaCl_2$ established by Haysom and Chapman (1975) for Si deficient in soils. Haynes and Zhou (2018) observed the lowest Si concentration at pH 8–9 which is the soil pH in the present study case.

The impact of the two types of amendment on available Si and its absorption by plants could vary because of their different effects on the chemical properties of soil due to their distinct characteristics (Table 4). The effect of the applied amendments was more clearly observed in the case of the irrigated soil under greenhouse conditions due to greater mineralization of the amendments. The NO_3^- values of the pellets and biochar were higher than the NO_3^- values of the original soil; therefore, significantly higher ($p < 0.01$) values of NO_3^- were measured in the soil with biochar and with pellets compared with the soil without amendment. The increased EC values of biochar and pellets compared with the values of the original soil could explain the higher values of SO_4^{2+} and Ca^{2+} in the soil with amendment. Finally, Si extracted by $CaCl_2$ was significantly lower ($p < 0.01$) in the case of soil with biochar than with pellets or without amendment (Table 3) which coincides with the lowest Si percentage found in the studied biochar (Table 4). In addition, biochar could be providing extra specific surface area that is beneficial for absorbing/adsorbing the available Si that was in the soil (Verheijen et al., 2010).

4.2 | Barley plant

The concentrations of Si obtained for barley ranged from 0.38% to 1.38% in dry weight. According to the categorization given by Takahashi et al. (1990), barley would be high Si (1–10%) or intermediate Si (0.5%–1%) accumulator plants depending on the case. However, the plants would be intermediate Si accumulator plants or even low Si accumulators (<0.5%) when they were cultivated under more favourable conditions such as in the greenhouse. The Si in barley grown in soil with irrigation under greenhouse conditions is lower than that measured in barley grown in rainfed field conditions (Figure 2). This coincides with the biomass values and could be related to a greater leaching. The present results differ from those published by Woli et al. (2011) who found a positive correlation ($R^2 = 0.32$, $p < 0.036$) between Si concentration in Miscanthus and precipitation. However, Woli et al. (2011) compiled data for plants grown in different types of soils, but none rich in $CaCO_3$ and this could be a reason for the contrasting results.

The different treatments (soil without amendment, with biochar and with pellets) showed there was significant correlation between available soil Si and plant Si (Table 6) and between plant Si and plant biomass ($\tau = 0.83$, $p < 0.01$; $\tau = 0.74$, $p < 0.01$ and $\tau = 0.67$, $p < 0.01$, respectively). In this case, the best plant biomass results, the greatest number of ears and the greatest grain weight were obtained for the soil with pellet amendment (Table 5). Moreover, plants have the highest Si uptake and the highest N uptake in the soil with pellets. N in plants is essential for a proper plant growth and development which directly influence yield increase, but as our results show Si has also a significantly positive influence. There were significant correlations between biomass and N uptake ($\tau = 0.75$, $p < 0.01$) and biomass and Si uptake ($\tau = 0.88$, $p < 0.01$).

The concentration of plant-available Si can influence the availability of nutrients in the soil and nutrient concentrations in plants. For example, there were significant negative correlations between P concentrations in plant and available Si ($\tau = -0.36$, $p < 0.01$) and between P uptake and available Si ($\tau = -0.47$, $p < 0.05$), which could be related to the deposition of Si in the roots and/or Si-induced decrease of transpiration rate as reported by Ma and Takahashi (2002). Likewise, the results showed significant higher N concentrations ($p < 0.01$) in barley grown in the soil with lower Si concentration (greenhouse irrigated soil) as shown in Figure 2. This corresponds to the work carried out by Yoshida et al. (1959) and other researchers such as Okuda and Takahashi (1965) or Ma and Takahashi (1990) which found N and P increase in rice when Si concentrations decreased in soils. Ma and Takahashi (2002) determined lower values of N and P in barley grown in soils enriched with Si, and Liu et al. (2014) found a N increase in cucumber fruit when soil Si concentrations decreased. In the present study, the lower N and P concentration in barley also coincided with the soil under drought conditions (rainfed soil) which generally limits total nutrient uptake and diminishes tissue concentrations in plants. Furthermore, this could be related to limited availability of energy for assimilation of NO_3^-/NH_4^+, PO_4^{3-} and SO_4^{2-} under drought conditions. A reduced transpiration rate due to water deficit reduces the nutrient absorption and efficiency of their utilization (Farooq et al., 2009). However, our results showed that N uptake was significantly higher in barley grown in soil with a greater Si concentration (field rainfed soil) unlike the case of N concentration (Figure 2). Another aspect to point out is that the greater the N uptake the greater the Si uptake ($\tau = 0.68$, $p < 0.01$). Therefore, Si could improve N use efficiency within the plant as observed by Detmann et al. (2012) in the case of rice.

In summary, the present study findings show that the rainfed soil with compost pellets with higher plant-available Si concentration had the greatest increase of the following: plant biomass; number of ears, grain weight, N uptake, Si concentration in plant and Si uptake.

4.3 | Soil–plant system

The soil properties that most strongly influenced Si accumulation in barley in all datasets were plant-available Si and N-Kjeldahl. The latter property was strongly, but negatively related to the barley Si. If we consider that N-Kjeldhal excludes NO_3^-, NH_4^+ is the form within N-Kjeldhal that plant could absorb. Therefore, it could be hypothesized that when more NH_4^+ is present in the soil, less plant-available Si is in the soil and therefore less Si will be accumulated in the plant. The reason is that this could be caused by ion absorption competition. Tsujimoto et al. (2014) suggested that using N fertilizer resulted in a reduction of Si concentration in rice straw which agrees with the results. But other factor could be also relevant. Considering that deprotonation of the silanol groups (Si-OH) on the phytolith surface can facilitate the water molecules to attack Si-O-Si bonds, Nguyen et al. (2014) carried out batch experiments with different electrolytes in synthetic soil solution and reported that neutralization of deprotonated $Si\text{-}O^-$ sites by anions and cations might accelerate polymerization leading to smaller Si release in comparison with absences of electrolytes. Our results showed that more NH^{4+} (N-Kjeldhal) in soil resulted in less plant-available Si which confirms this finding in the soil under field and greenhouse conditions.

In the case of the highly calcareous soil with phytolithic biochar, OM was another important property positively related to the plant Si content. The OM from phytolithic biochar is an important reservoir of biogenic Si since it is composed mainly of plant-derived amorphous Si although minor pools of zoogenia, microbial, protistic Si also exist (Haynes, 2017). Moreover, the study showed that phytolithic biochar (pyrolysed at 750ºC) had a high stability towards decomposition in soil and it has a constant feed flow based on a slow release of nutrients resulting in a long-term effect for available Si. Therefore, a gradual supply of OM by phytolithic biochar seems to be an important source of plant-available Si. These results are in agreement with authors such as Rizwan et al. (2019); or Abe et al. (2016) who observed this in soils with a pH > 6.5.

In the case of the highly calcareous soil with pellets, there was also a relevant positive relation of pH and negative relation of Ca^{2+} and EC with Si content in barley. Considering a pH range between 8.0 and 8.4, the results showed that an increase in soil pH increased the available Si in soil and the accumulation of Si in barley which was also reported by Meunier et al. (2018) for pH values up to 7.5. Haynes and Zhou (2018); and Tavakkoli et al. (2011) reported contrary results in soils whose pH values ranged between 5.0 and 7.1. However, our results agree with those of Haynes and Zhou (2018) which also obtained a positive relationship between pH and Si extracted by $CaCl_2$ in soils using blast furnace slag amendment where the pH values ranged between 4.9 and 7.0. Moreover, considering that Si supply by pellet is biogenic, our results coincide with those of Fraysse et al. (2006) where the dissolution of biogenic Si strongly increases with increasing pH. Our results suggest that if an organic amendment with a lower pH is added to calcareous soil, the pH increases, because the soil buffer capacity will favour the mentioned Si dissolution. Li et al. (2018) observed similar results in experimental works where Si was supplied through the addition of phytolithic biochar. They observed increases of available Si as pH conditions enhanced phytolith solubility which depended on the soil buffering capacity. Regarding Ca^{2+} and EC, the studied pellets supplied large amounts of ions which could decrease their availability and/or change the soil chemistry (precipitation, ion competition and ion affinity for adsorption sites of soil constituents). This could have a compensation effect in Si absorption competition. Furthermore, as in the case of N-Kjeldhal, our results of a negative relation between Ca^{2+} and EC with plant-available Si are in agreement with the findings of Nguyen et al. (2014).

5 | CONCLUSIONS

This study found that Si availability in the highly calcareous soil had a direct positive effect on Si absorption by barley plants and on its resulting biomass. In addition, more favourable conditions for cultivation seem to change the role of Si in the soil–plant system. For example, Si absorption and N uptake were lower than those in the rainfed soil whereas the P absorption was higher. Barley Si concentration, Si uptake and available-Si in highly calcareous soil were affected by other factors which were observed when performing the PCR analysis. A strategy to improve Si absorption by barley plants under field conditions and, consequently, biomass would be to use organic amendments that are enriched with Si and/or that mainly supply N in a form other than NH^{4+}. The results showed phytolitic biochar is a reservoir of biogenic Si because of its plant-derived OM and can act as a gradual release source of Si. Another important factor to consider is that a pH increase in the highly calcareous soil induces dissolution of the biogenic Si pool. Furthermore, high inputs of Ca^{2+} and other electrolytes that increase the EC should be avoided in order to maintain the dissolution rate of biogenic Si. In the case of N ions, the results suggest that Si presence could improve N use efficiency within the plant which in turn would increase the plant biomass. Si is involved in biochemical processes, but also seems to be involved in physiological processes. Therefore, further studies will be required to focus on the chemical reactions between plant-available Si and different ion concentrations in plant and highly calcareous soil system when an ion rich amendment is applied.

To sum up, increasing plant-available Si in highly calcareous soil, and as a consequence barley Si absorption, has important implications for improving production and global food security. This also has far reaching effects regarding sustainable agriculture within marginal lands which are becoming important alternatives for possible food production as demand increases.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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