Exploring the impact of external H$_4$SiO$_4$ addition on three Mediterranean agricultural soils

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INTRODUCTION

The increasing global population requires increased crop productivity to meet food demands, prompting interest in biostimulants with low environmental impact. Among these, silicic acid (H$_4$SiO$_4$), the bioavailable form of silicon, has emerged as a promising agent for alleviating both biotic and abiotic stresses in crops (Epstein, 2005). Its effectiveness has been observed not only in mitigating environmental stresses such as drought but also in reducing the toxicity of heavy metals like cadmium (Cd) and zinc (Zn) by decreasing their bioavailability (Cunha et al., 2008). Despite the undeniable abundance of silicon (Si) in the environment, there is a significant deficiency of Si in its bioavailable form in soils, limiting its potential benefits for crops (Paye et al., 2018). Understanding the dynamics of silicic acid in soils is crucial to harness these benefits effectively. However, the behaviour and dynamics of silicic acid in soils remain poorly understood, particularly at high pH levels (>9), where polymerization processes can significantly limit its availability for plant absorption (Babu et al., 2016). Furthermore, interactions with various soil fractions may influence its adsorption and ultimately its bioeffectiveness. Despite the mechanisms underlying silicic acid's interaction with the soil and heavy metals are not yet fully understood, the addition of silicic acid as an external source of silicon holds considerable promise for enhancing crop yield and resilience. This research aims to understand how silicic acid interacts with soil fractions and how adding an external source impacts its concentration in soil solution. This knowledge will help optimize its use in reducing crop stress and supporting sustainable agriculture, especially in metal-contaminated areas.

MATERIALS AND METHODS

The silicic acid used in this study was in its pure form, supplied by Sigma-Aldrich, with a high purity of >99.9%. The experimental solubility of silicic acid in this experiment was 1 mg/l. The reported pK_{a1} for the compound is 9.8. Three Mediterranean agricultural soils from the southwestern region of Spain were selected to study the effect of the addition of silicic acid to soils, each with different physicochemical characteristics (Table 1). The pH, texture, and organic matter content variability was particularly noteworthy. Soil samples were collected from the surface layer between 0 and 20 cm depth.

Soil	Texture	Sand (%)	Silt (%)	Clay (%)	CaCO$_3$ (%)	OC[a] (%)	Total N (%)	pH[b]
S1	Sandy Loam	76 ± 1	9 ± 1	15 ± 1	1.9 ± 0.1	0.80 ± 0.06	0.10 ± 0.01	8.4 ± 0.1
S2	Clay	18 ± 1	28 ± 1	44 ± 1	49.5 ± 0.6	0.42 ± 0.01	0.06 ± 0.01	8.5 ± 0.1
S3	Loam	46 ± 1	38 ± 1	16 ± 1	< 0.20	3.50 ± 0.12	0.40 ± 0.01	5.5 ± 0.1

a organic carbon. b measured in 1 g:2.5 ml soil:water

Table 1. *Physicochemical properties of the soils used in this work.*

The procedure was conducted as follows: 1 g of soil was placed in 40 mL polypropylene centrifuge tubes, and then 25 mL of a 1 ppm H$_4$SiO$_4$ solution was added and agitated for 96 hours at 20°C (Babu et al., 2016). Prior to this, the soils were sterilized three times in an autoclave at 121°C and 200 kPa to prevent any biodegradation. Following

this, the tubes were centrifuged at 10,000 rpm for 15 minutes. The supernatant was filtered through a 0.45 μm filter, acidified to 2% with HCl, then measured by ICP-OES. The effect of silicic acid supplementation was determined by the difference between soil samples treated with silicic acid and soil samples treated with water (blanks). This approach allows for the evaluation of changes in silicic acid concentration in the soil due to its external addition, thus avoiding potential erroneous readings caused by the natural silicic acid content in these soils. All procedures were performed in triplicate.

RESULTS AND DISCUSSION

The addition of silicic acid to the soils yielded varying results depending on the soil type in relation to the amount of silicon in solution. A decrease in the concentration of silicon was observed compared to the blanks, in the following order: S1 > S2 >> S3, as illustrated in Fig. 1a. The Pearson correlation coefficients revealed a significant negative correlation between the decrease in this concentration and the silt content ($r = -1.000$, $P = 0.009$). This finding is confirmed by performing a linear regression between the silt content and the loss of silicon in solution (Fig. 1b), resulting in an $R^2 = 0.999$ for the line relating the two variables.
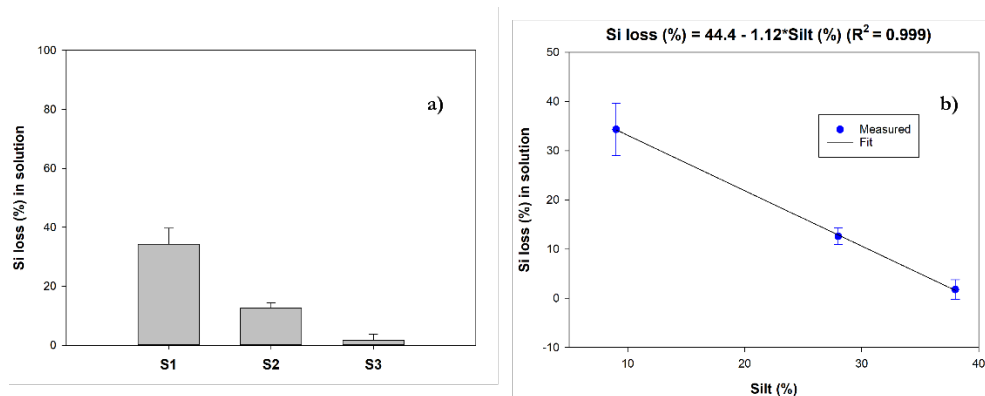

Fig 1. *a) Silicon loss in solution compared to blanks in soils (S1-S3). b) Linear regression for Si loss values using the silt content of the soils as the predictable variable.*

Although the adsorption values of silicic acid could not be evaluated in this study, it is observed that in soils with higher pH there is a lower concentration of Si in solution. This may be directly related to the pH levels. Babu et al. (2016) have found that at pH levels above 8, silicate ions tend to adsorb to the soil. Additionally, pH-dependent reactions occur that regulate the adsorption of these ions, which may explain the decrease in the concentration of Si in the soil solution. Further research is needed to understand the interactions of silicic acid with soil fractions and crops to assess its real potential as a biostimulant.

ACKNOWLEDGMENTS

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