



Foliar application of natural zeolites affects the growth and productivity of processing tomato

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ABSTRACT

The foliar application of zeolites has been proven to positively affect plant physiology suggesting that it could improve plant growth, however, this topic has been little studied. Two field trials were carried out (in 2021 and 2022) to study the potential beneficial effect of natural zeolite particle films on processing tomato crops. Natural zeolites i) clinoptinolite + and mordenite (CubZeo) and ii) micronized clinoptinolite (BigZeo) were sprayed onto the plants six times in the central crop cycles. In both trials, BigZeo promoted leaf and fruit dry mass (DM) accumulation, and leaf area from the early crop stage compared to the water-sprayed plants (Control). The final aerial DM of BigZeo plants enhanced more in the year with favourable (+39.2%) (2022) than in that with more stressing thermal conditions (2021) (+12.1%). Concurrently, the marketable yield was improved by +36% in both years with positive effects also on fruit total soluble solids. Under heat stress, the CubZeo crop showed even lower aerial DM than the Control, however, the marketable yield remained similar due to higher fruit DM and higher incidence of blossom-end-rot (BER) in untreated plants. In 2022, CubZeo promoted DM accumulation, leaf expansion and yield even if to a lesser extent than the BigZeo treatment. In the fruits the concentrations of K, Ca, and Mg rose in zeolite-treated plants. The improved Ca level in the fruits can explain the lower occurrence of BER in the zeolite-treated plants, particularly with CubZeo. Si was observed at the highest level in fruits and stems of BigZeo-treated plants, followed by CubZeo and Control ones. The accumulation of Si could explain the best crop responses elicited by BigZeo, whereas the observed responses did not appear to involve changes in the photosynthetic machinery. However, further and comprehensive investigations are needed to define the zeolite film particle characteristics and the related physiological and nutritional changes in the plants.

1. Introduction

Natural zeolites are formed at sites of volcanic activity on an island or in coastal areas. Depending on their origin the type of minerals present in them may differ (Jarosz et al., 2022). The best-known natural zeolites are clinoptinolite, chabazite, mordenite, stilbite, erionite, heulandite, and phillipsite (Ramesh and Reddy, 2011).

Zeolites are hydrated aluminosilicates that are characterized by a tetrahedral structure of SiO₄ and AlO₄ joined by the sharing of all oxygen atoms. Cavities and channels inside the aluminosilicate framework, generating a nanohoneycomb structure (Constantinescu-Aruxandei et al., 2020), hold cations along with the water molecules which can be reversibly removed (Reháková et al., 2004). As zeolites are nanoporous solids (Jarosz et al., 2022), specific features are reported for these materials, such as selectivity of adsorption towards specific chemicals and

ions, high molecular-sieve properties, regenerability and modifiability of sorption capacity. For this reason, they are widely used for industrial applications, ecology and environmental protection, remediation, veterinary, medicine and agriculture (Jarosz et al., 2022).

Agricultural use of zeolites involves application i) as a soil amendment, ii) as a carrier for slow release of herbicides and fertilizers, iii) to protect crops from pests and diseases, iv) in aquaculture and animal feed additive (reviewed by Reháková et al., 2004; De Smedt et al., 2015; Eroglu et al., 2017; Jarosz et al., 2022).

Especially in herbaceous crops, it has been proved that soil application of zeolites results in yield increase mainly involving plant mineral and water nutrition (Noori et al., 2006; Ghannad et al., 2014; Tsintskaladze et al., 2017; Baghbani-Arani et al., 2020; Sedaghat et al., 2022), and photosynthetic activity (Zheng et al., 2018; Chatzistathis et al., 2021).

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More recently, the foliar application of zeolites has been studied as a sustainable approach for the control of pests (De Smedt et al., 2016; Rotondi et al., 2021; Baghodrat et al., 2021) and diseases (Calzarano et al., 2020) due to zeolite reversible dehydration, and the formation of a film particle (De Smedt et al., 2015; De Smedt et al., 2016; Rotondi et al., 2021; Moale et al., 2021). Furthermore, some of these studies, mainly involving tree crops, report the zeolite particle film affecting i) leaf characteristics [both physiological (Rotondi et al., 2021; Valentini et al., 2021; Moale et al., 2021) and optical (Calzarano et al., 2020; Moale et al., 2021)], ii) product quality (Calzarano et al., 2020; Rotondi et al., 2021; Valentini et al., 2021; Moale et al., 2021) and iii) product shelf-life (Huwei et al., 2021). Overall these findings suggest the use of foliar application of zeolites as a potentially innovative approach to mitigate the effects of climate change in agriculture by contrasting water/high-temperature stress (Valentini et al., 2021; Jarosz et al., 2022).

Many issues are arising for vegetable crop productivity due to climate change (Bisbis et al., 2018), and specifically for processing tomato crop, a projected (2010–2040 period) increase of 0.8–2.4 °C in air temperature have been reported to cause a 15% reduction in yield (Camarano et al., 2020). Tomato (*Solanum lycopersicum* L.) is one of the most important vegetables in the world and Italy, in particular, is one of the major producers of processing tomatoes (13% of worldwide production in 2020, 3.9 million metric tons) (World Processing Tomato Council, 2020). The Puglia region is the second most important Italian area for processing tomato production (more than 17,000 ha grown annually, concentrated in Foggia province) (ISTAT, 2022).

To date, the leaf-coating effects of zeolite on crop growth and yield are still little known, especially for vegetable crops, despite several commercial producers advertising the growth-promoting properties of leaf-applied zeolites, along with crop protection efficiency. It has been suggested that since zeolites can adsorb carbon dioxide, an enhanced level of CO₂ close to the stomata could result in improved leaf photosynthesis and, as a consequence, plant growth and productivity (De Smedt et al., 2015). De Smedt et al. (2017) proved a tendential increase in growth for apple and tomato plants, however, higher net photosynthesis was only observed for apple leaves. This response was not proved in the studies performed on olive and grapevine (Rotondi et al., 2021; Valentini et al., 2021). Another hypothesis is based on the potential alleviation of high-temperature stress of the zeolite particle film resulting in improved crop performance (De Smedt et al., 2015; Cataldo et al., 2021) which was not confirmed for grapevine (Valentini et al., 2021), apricot or peach (Moale et al., 2021). In the latter studies, the foliar application of zeolite rather showed an increase in anthocyanins (grape) and polyphenols (apricot and peach), suggesting a response involving secondary metabolism. No published studies are available about the effect of zeolite foliar application on crop nutritional status, however, since zeolite coatings affect crop physiology, it can be hypothesized they might also modulate mineral uptake. Moreover, information is lacking on the zeolite coating effect on silicon plant nutrition, though zeolites are reported to produce soluble silicon (Constantinescu-Aruxandei et al., 2020; Moale et al., 2021) which is a plant biostimulant (Laane, 2018).

Based on these considerations, the present study aims to improve knowledge about the potential beneficial effects of natural zeolite particle films on processing tomato crop growth and productivity, focusing on the plant nutritional aspects not previously exploited to date. With this objective, two natural zeolite-based products were tested as a foliar spray on tomato crops to mainly assess the dry biomass accumulation and partitioning, yield parameters and nutrient concentrations.

2. Materials and methods

2.1. Experimental setup

Two field trials were carried out in 2021 (exp. 1) and 2022 (exp. 2)

on a commercial farm (41° 25' N 15° 23' E, 175 m asl-exp. 1; 41° 25' N 15° 22' E 179 m asl-exp. 2), located on the Capitanata Plain in Foggia province, Puglia region (Southern Italy). This plain (about 400,000 ha) is mainly cultivated with durum wheat which is grown in a 3–4 year rotation with processing tomato and other vegetable crops. The selected commercial farm is representative of the soil and climate conditions in the area, dominated by a Mediterranean climate with a mild winter and a hot dry summer (Elia and Conversa, 2012).

The experimental fields used in the 2021 and 2022 trials were contiguous with each other, with soils having the following respective characteristics: sand, 40.3/38.1%; loam, 33.7/38.5%; clay, 26.0/23.4%; organic matter, 3.0/3.2%; total N (Kjehldahl) 0.165/0.201%; Olsen P, 47.8/50.8 ppm; extractable K, 300.8/308.3 ppm; pH 7.9 (soil:water 1:2.5), active carbonate 0.07/0.13%, CEC 29.6/36.2 meq 100 g⁻¹ and C/N 9.7. In both trials, the preceding crop was broccoli [*Brassica oleracea* L. conv. *botrytis* (L.) Alef. var. *cymosa* Duch.].

Before transplanting, 500 kg ha⁻¹ of triple superphosphate fertilizer (46%) (Perfosfato triplo 46%, Fertilisud s.r.l., Spinazzola (Barletta-Andria-Trani, Italy) and 100 kg ha⁻¹ chicken manure (4/3/3) (Italpolina, Hello Nature Italia s.r.l., Rivoli Veronese, Verona, Italy) were applied and incorporated into the soil. Mineral fertilizers were also provided during the May - July period through fertigation. Fertilizers used were: urea phosphate (17.5–44) (Haifa UP, Haifa Italia s.r.l., Bologna, Italy), ammonium nitrate (34.2) (YaraTera Amnitra, Yara Italia s.p.a., Milano, Italy), phosphoric acid (54%) (Fosforo 54, Biolchim s.p.a., Medicina, Bologna, Italy), Solinure® GT (10–5–39) (ICL Italy s.r.l., Milano, Italy). As a whole, a total of 260, 300, 105, and 148 kg ha⁻¹ of N, P₂O₅, K₂O and SO₄, respectively, was applied.

The transplanting of processing tomato (*Solanum lycopersicum* L.), cv. Taylor F1 (Nunhems Italy –BASF, Vegetable seeds, S. Agata Bolognese BO, Italy), an oblong-shaped fruit typology, was carried out on May 8th 2021 and on May 23rd 2022 (at the 4th true-leaf stage). Plantlets were spaced in twin rows 40 cm apart, with 50 cm between the rows, and 1.7 m between the double rows (density 2.9 plants/m²).

Crop water requirements were completely satisfied by drip irrigation (drip tube – Agrifim, in-line emitters, 1.6 L h⁻¹, spaced at 0.3 m) until one week before harvesting. Irrigation (5.300 and 4.400 m³ ha⁻¹ in exp.1 and exp. 2, respectively) and N fertigation were based on recommendations provided by a decision support system (DSS) named GesCoN (Elia and Conversa, 2015; Conversa et al., 2015) using the EcoFert web platform (<https://www.ecofert.it/>) and its smartphone application (Gallardo et al., 2020; Elia et al., 2021). Weeds, pests and diseases were controlled according to the regional integrated pest management rules. Specifically, in exp. 1, we performed six applications of fungicides, four applications of insecticides, and one application of acaricides. In the second trial, these applications were adjusted to eight, four, and zero, respectively. Weather conditions during the two growing seasons are reported in Fig. 1.

2.2. Treatments and experimental design

Natural zeolites i) Cuban zeolite (CubZeo) (Bioagrotech s.r.l., Republic of San Marino) and ii) Big-Zeo (BigZeo) (Agricola Internazionale s.r.l., Pisa, Italy) are commercially manufactured products. Cuban zeolite contains clinoptinolite (67,5%) and mordenite (32,5%) and BigZeo contains clinoptilolite (91%). The two natural zeolites also differ in particle dimensions (< 40 µm and D50 < 6 µm for the Cuban zeolite and Big-Zeo, respectively) with BigZeo being a micronized type. More details about the mineralogical and physicochemical characteristics of both zeolites are reported in Table A.1.

Zeolite applications were performed by spraying tomato plants with an aqueous solution (500 L ha⁻¹) containing 5 kg of zeolites (according to the guidelines provided by the producer) using tractor-mounted field sprayers, equipped with a 38 Albuz nozzle (ATR 80-green, Pentair Hypro, Cambridge, UK) boom (18 m long). On Control plants, only water was used.

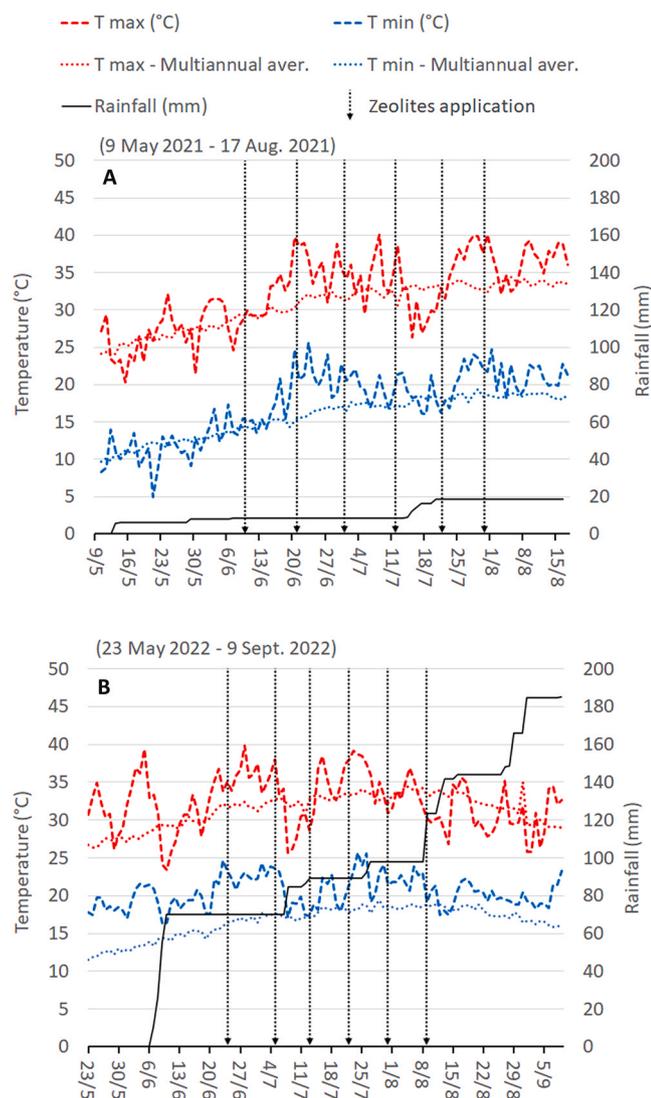


Fig. 1. The daily temperatures (the minimum, maximum, and multiannual averaged values) and rain events during the 2021 (A) and 2022 (B) crop cycles. The dotted lines indicate the dates of zeolite application: 32, 44, 54, 65, 75 and 84 DAT, 2021; 32, 43, 51, 60, 69, 78 DAT, 2022.

For each experiment, the CubZeo, BigZeo and Control treatments were arranged in a randomized block design with four replications. The experimental plot unit included 11 double rows and was 18 m wide and 30 m long.

Starting from nearly 30 days after the transplant (DAT), zeolite applications were performed six times namely, in 2021 on June 10th and 21st, July 1st, 12th, 22nd, and 31st (32, 44, 54, 65, 75 and 84 DAT, respectively) (exp. 1) and in 2022 on June 24th, July 5th, 13th, 22nd, 31st and August 9th (32, 43, 51, 60, 69, 78 DAT, respectively) (exp. 2).

2.3. Plant sampling and measurements

During the two growing seasons, from the five innermost double-rows of the experimental plot unit, five plants were randomly sampled (twin-row borders were not considered) at 31, 62, 95 DAT and 36, 64, 80, 105 DAT, in exp. 1 and 2, respectively. The fresh weight of aerial parts (leaves, stems, and fruits) was determined and the leaf area was measured using a leaf area meter (Li-3100, Licor, Lincoln, NE, USA). To determine the dry weight, a portion of fresh leaves, stems and fruits was dried in a thermo-ventilated oven at 70 °C until it reached a constant mass. The dry matter (DM) concentration was calculated as [(dry

weight/fresh weight)* 100].

The index effectiveness (IE) (Conversa et al., 2013) of the zeolite treatments was calculated on aerial dry mass (gIE) at 95 (exp. 1) and 105 DAT (exp. 2) as:

$$gIE_{BZ} = (\text{BigZeo aerial DW} - \text{Control aerial DW}) / \text{BigZeo aerial DW} \times 100.$$

$$gIE_{CZ} = (\text{CubZeo aerial DW} - \text{Control aerial DW}) / \text{CubZeo aerial DW} \times 100.$$

At 65 DAT in exp. 2, five days after the 4th zeolite application, leaf gas exchange and chlorophyll fluorescence measurements were carried out. Photosynthetic rate (A_n), stomatal conductance to H_2O (g_s), intercellular CO_2 concentration (C_i), transpiration rate (E), and the efficiency of PSII (PhiPS2) were measured using an open circuit infrared gas exchange system for leaf gas exchange measurements fitted with a leaf fluorimeter and a LED light source, model Li-6400XTF (LI-COR Inc., Lincoln, NE, USA), on a fully expanded leaflet of 5 plants per plot of the randomized block design. The leaf temperature was kept at 33.5 °C, CO_2 concentration at 400 $\mu\text{mol mol}^{-1}$ of air and the actinic light at 1500 $\mu\text{mol m}^{-2} \text{s}^{-1}$.

At harvest, performed at 102 and 109 DAT in exp. 1 and 2, respectively, the number and fresh weight of the fruits classified as marketable, unripened and unmarketable (showing blossom-end-rot symptoms) were assessed on 20 randomly selected plants per experimental unit. Colour indices were measured on commercial fruits. They were based on the $Cie L^*a^*b^*$ scale 1976- L^* , indicating lightness/darkness, ranging from 0 (black) to 100 (white) value in a greyscale; a^* reflecting greenish (if negative) to reddish (if positive) tonality; b^* indicating bluish (if negative) to yellowish (if positive) tonality. They were performed on the images taken using the image acquisition station created by Immagini & Computer s.n.c. (Bareggio, MI, Italy), equipped with: 4 white Tornado ESaver (23 W) lamps (Philips s.p.a., Milano, MI, Italy); a Nikon D5200 camera (Nikon Corporation, Tokyo, Japan); and Image Pro Plus 7.0 software (Media Cybernetics Inc., Rockville, MD, USA). In addition, the hue angle (h_o) and chroma index (C^*) were evaluated.

2.4. Chemical determinations

The nitrogen, phosphorus, inorganic cations and silicon concentrations were analyzed on dried plant material collected at the last sampling (leaf, stem, fruit) of exp. 1, exp. 2, and milled through a 1.0 mm sieve (IKA Labortechnik, Staufen, Germany). Fruit samples (40 per experimental unit) before drying were carefully washed with distilled water for chemical determinations.

Nitrogen was determined through dry combustion (Dumas method) using a CHN Elemental Analyzer (FlashEA 1112, ThermoFisher Scientific, Waltham, MA, USA). Phosphorus was determined through the molybdenum-blue method using a spectrophotometer (Shimadzu UV-1800, Shimadzu Scientific Instruments, Columbia, MD, USA) and the procedure described in Conversa et al. (2013).

Inorganic cations were analyzed by ion chromatography (Dionex ICS 3000; Dionex, Sunnival, CA, USA) according to the method reported by Bonasia et al. (2010). Briefly, they were extracted from dried samples (1 g), previously ashed (in a muffle furnace at 550 °C for 6 h) and acid digested (20 mL of 1 mol L^{-1} HCl in boiling water for 30 min), before injection into the ion chromatography system. The ion chromatography system was equipped with an isocratic pump, a conductivity detector, an auto-sampler model AS-DV (ThermoFisher Scientific, Waltham, MA, USA), a self-generating DRS-600 suppressor (4 mm), a Dionex IonPack CS12A analytical column (4 × 250 mm, 5 μm), and an eluent solution (20 mM methanesulfonic acid) at a flow rate of 1 mL min^{-1} (Dionex-ThermoFisher Scientific, Waltham, MA, USA).

For the determination of Si concentration, 0.3 g of dried samples were ashed in a muffle furnace at 550 °C and digested with 20 mL of 1 mol L^{-1} HCl in boiling H_2O (95 °C) for 30 min. The resulting solution was filtered, diluted and analyzed by spectrophotometry method (ASTM D859: Standard Test Method for Silica in Water). The solutions required

for this procedure were ammonium molybdate solution 7.5 g ((NH₄)₆Mo 7 -O₂₄ 4 H₂O) in 100 mL of water, oxalic acid solution (H₂C₂O₄ 2 H₂O) at a concentration of 10 g L⁻¹, 18% hydrochloric acid solution. The reducing solution consisted of 30 g of sodium hydrogen sulfite (NaHSO₃), 1.5 g of sodium sulfite (Na₂SO₃), and 0.5 g of 1-diazo-2-naphthol-4-sulfonic acid (H₂NC₁₀H₅(OH)SO₃H) dissolved in 200 mL of H₂O. Five mL of sample or standard, 100 µL of the HCl solution and 200 µL mL of (NH₄)₆Mo 7 O₂₄ 4 H₂O solution were added in rapid succession. The solution was mixed and allowed to sit for 5 min 150 µL of oxalic acid was added and allowed to sit for 1 min; then 200 µL of the reducing solution was added, and the solution was allowed to sit for 10 min. The absorbance of the samples was determined at 640 nm (Shimadzu UV-1800, Shimadzu Italia S.r.l. Milano, Italia). The quantification of Si in extracts was performed by interpolation with a calibration curve.

On commercial fruits, Total Soluble Solids (TSS) were assayed using the refractometric method (digital refractometer DBR35, Giorgio Bormac s.r.l., Carpi, Italy), according to the method given in Association of Official Agricultural Chemists (AOAC) (Method No. 932.12) (AOAC, 2000). To measure pH, a fresh sample (10 g) was blended in 100 mL of distilled water. The pH was measured using a pH meter (Hanna Instruments Italia s.r.l., Villafranca, Italy).

Total titratable acidity was determined according to the method No. 942.15 given in AOAC (AOAC, 2000). Fresh samples were homogenized in a blender and then passed through filter paper. The filtrate was diluted with distilled water and the pH was measured (Hanna Instruments Italia s.r.l., Villafranca, Italy). The same filtrate was then titrated with 0.1 N NaOH solution up to an end-point of pH 8.2. The result is expressed as grams of citric acid per 100 g of fresh weight.

2.5. Statistical analysis

All data were statistically analyzed by ANOVA carried out using GLM (General Linear Model) procedure - SAS software. The Tukey's Honestly Significant Difference (HSD) Test ($\alpha = 0.05$) was used to establish differences between means.

3. Results

3.1. Climatic conditions

The maximum and minimum daily temperatures averaged over the cultivation period, were 32.4 °C and 19.3 °C in 2021 (May 9th –Aug. 17th) and 32.4 °C and 20.4 °C in 2022 (May 23rd–Sept. 9th), respectively. However, in experiment 1 from 40 to 63 DAT and from 74 DAT up to harvest, maximum temperatures were higher than 35 °C, frequently reaching values close to 40 °C (Fig. 1A). In the 2022 trial, high maximum temperatures (above 37 °C) for two or more subsequent days (heat-waves) rarely occurred (Fig. 1B). During the 2021 trial rainfall was very low (18.7 mm), whereas it was much higher (185.3 mm) in the following trial with a concentration in the last two months of the crop cycle (fruit development phase).

3.2. Crop growth and yield

Statistical analysis, performed on crop growth and yield data, including those reported in paragraph 3.3, highlighted a strong significant 'year' effect (Table A. 2). As a result, the findings were presented separately for each respective year.

In experiment 1, the differences in the total aboveground dry mass accumulation (DM) between treatments [micronized clinoptilolite (BigZeo), clinoptilolite + mordenite (CubZeo) or treated with water (Control)] appeared starting from 30 DAT. Specifically, up to 62 DAT the aerial DM was similar in BigZeo and CubZeo plants and both had higher values ($P \leq 0.01$) compared with the Control (Fig. 2 A). Subsequently, the CubZeo plants showed a slower increase in DM accumulation than

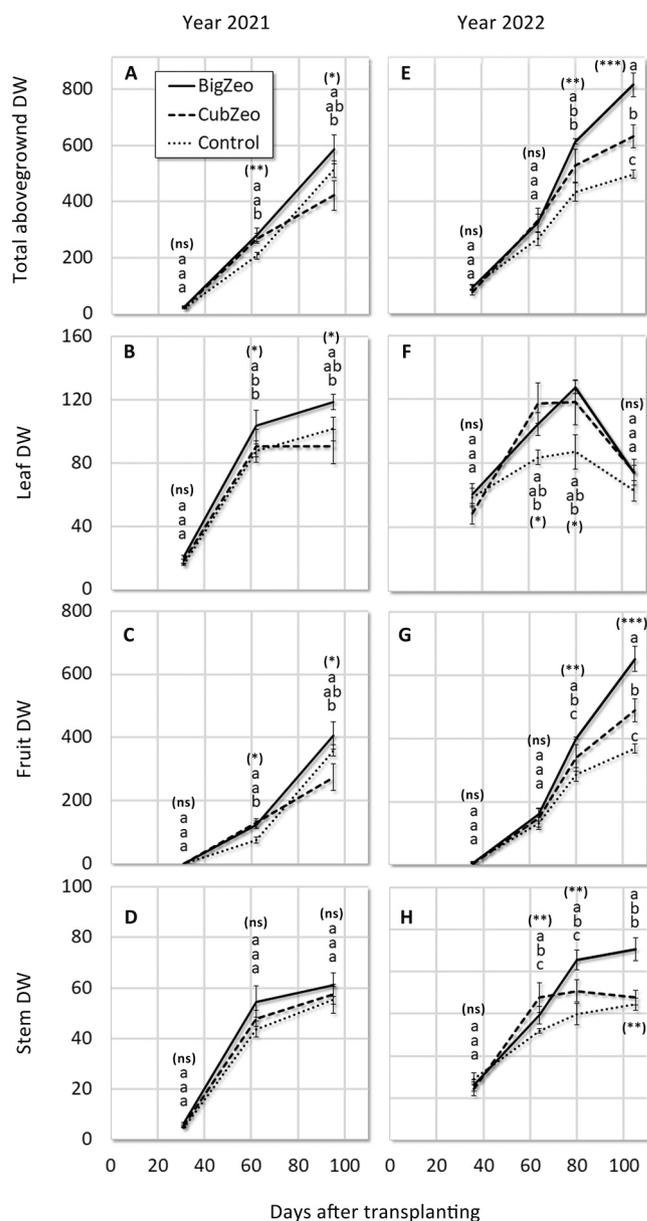


Fig. 2. Total, leaf, fruit and stem dry mass accumulation (g/plant) in 2021 (A, B, C, D, respectively) and 2022 (E, F, G, H, respectively) processing tomato trial as affected by foliar application of Cuban zeolite (CubZeo) and micronized clinoptilolite (BigZeo). Bars indicate \pm SE of mean ($n = 4$). Different letters indicate significant differences according to the Tukey test ($\alpha = 0.05$). Notations: ns, *, **, and ***, not significant or significant at $P \leq 0.05$, $P \leq 0.01$, and $P \leq 0.001$, respectively.

the others, reaching a lower value ($P \leq 0.05$) (422 g per plant) at the end of the cycle (95 DAT), especially compared with the BigZeo crop (586 g per plant).

During the crop cycle, both leaf DM accumulation (Fig. 2B) ($P \leq 0.05$) and leaf expansion (LAI) ($P \leq 0.05$) (Fig. 3A) showed a higher increasing rate in BigZeo plants than in CubZeo and Control. Specifically, at the sampling before the harvest (95 DAT), leaf DM reached values of 119 g in BigZeo plants and 96 g, on average, in the others. Fruit dry biomass accumulation mirrored the pattern of the total DM, with higher final values for BigZeo ($P \leq 0.05$) (406 g per plant) than for CubZeo plants (274 g per plant) and intermediate for the Control ones (Fig. 2 C).

Stems DM was not affected by treatments (Fig. 2D).

In experiment 2, after 64 DAT the increase in total DM accumulation

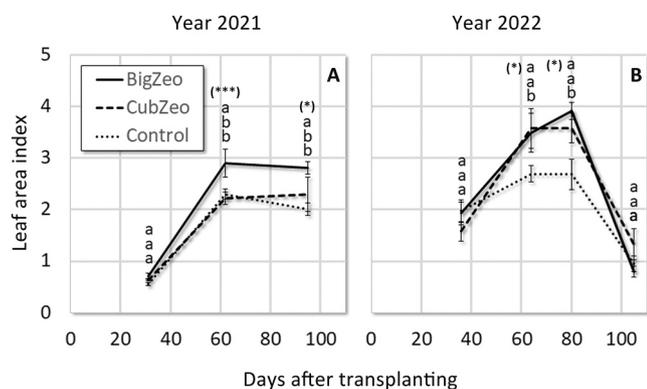


Fig. 3. Leaf area index in 2021 (A) and 2022 (B) processing tomato trial as affected by foliar application of Cuban zeolite (CubZEo) and micronized clinoptilolite (BigZEo). Bars indicate \pm SE of mean ($n = 4$). Different letters indicate significant differences according to the Tukey test ($\alpha = 0.05$). Notations: ns, *, and ***, not significant or significant at $P \leq 0.05$, and $P \leq 0.001$, respectively.

in zeolites-treated plants was sharper than the Control, particularly in the period 80 ($P \leq 0.01$) - 105 ($P \leq 0.001$) DAT in the BigZeo treatment (Fig. 2 E). The final aerial DM was 816, 631, and 496 g per plant in the BigZeo, CubZeo and Control plants, respectively. From 36 to 64–80 DAT, enhanced leaf DM accumulation (Fig. 2 F) and leaf expansion were observed (Fig. 3B) in the zeolite-treated compared with the untreated plants, followed by a reduction for all treatments in the period 80–105 DAT. A similar pattern was registered for DM of stems and fruits (Fig. 2 H, G). At the last sampling (105 DAT) ($P \leq 0.001$), the latter was 651, 489 and 368 g per plant in the BigZeo, CubZeo and Control plants, respectively, while stem DM was the highest in BigZeo treatment ($P \leq 0.01$).

In the 2021 trial, the foliar application of the BigZeo zeolite resulted in an improvement in fresh weight ($P \leq 0.01$) and number ($P \leq 0.05$) of commercial fruits compared with CubZeo and the Control. No differences emerged in the occurrence of unripe fruit and only CubZeo plants showed a lower weight ($P \leq 0.05$) and number ($P \leq 0.05$) of fruits affected by blossom-end rot (BER) (Table 1) while the incidence of BER on total production (marketable + unripe fruits) was 5.6%, 8.2% and 12.8% in CubZeo, BigZeo and Control plants, respectively.

In the second experiment, BigZeo plants gathered the highest commercial yield ($P \leq 0.001$) followed by the CubZeo and Control ones,

Table 1

Yield characteristics of processing tomato plants as affected by foliar application of two zeolite types in 2021 (experiment 1) and 2022 (experiment 2) field trials.

Treatments ²	Marketable		Unripen		BER		Dry matter
	(no.)	(g/plant)	(no.)	(g/plant)	(no.)	(g/plant)	(g kg ⁻¹ fresh weight)
Experiment 1							
BigZeo	71.3 a ⁽¹⁾ (± 5.2)	5011 a (± 331)	14.1 a (± 11.3)	729 a (± 196)	10.2 ab (± 4.7)	473 a (± 116)	49.5 ab (± 2.0)
CubZeo	60.6 b (± 3.8)	3808 b (± 302)	16.9 a (± 8.3)	726 a (± 381)	5.5 b (± 1.8)	255 b (± 88)	46.1 b (± 3.5)
Control	54.6 b (± 3.6)	3204 b (± 331)	14.1 a (± 3.7)	618 a (± 167)	17.2 a (± 3.4)	490 a (± 122)	60.1 a (± 2.0)
Significance ⁽²⁾	*	**	ns	ns	*	*	*
Experiment 2							
BigZeo	91.4 a (± 5.7)	5878 a (± 164)	18.2 a (± 4.6)	788 a (± 177)	16.7 a (± 1.2)	664 a (± 67)	55.5 a (± 1.3)
CubZeo	84.3 a (± 2.6)	5220 b (± 168)	9.0 a (± 2.6)	443 a (± 160)	8.3 b (± 1.3)	322 b (± 43)	50.5 b (± 1.7)
Control	54.2 b (± 4.4)	3813c (± 297)	17.3 a (± 4.0)	573 a (± 246)	8.7 b (± 2.4)	433 b (± 127)	50.7 b (± 3.0)
Significance ⁽²⁾	***	***	ns	ns	*	**	**

⁽¹⁾ Different letters within the column indicate significant differences according to the Tukey test ($\alpha = 0.05$)

⁽²⁾ ns, *, and **, not significant or significant at $P \leq 0.05$, and $P \leq 0.01$, respectively.

² BigZeo: Micronized zeolite Big-Zeo, Agricola Internazionale, s.r.l.; CubZeo: Cuban zeolite, Biogrotech s.r.l.

whereas both the zeolite treatments had a higher number of marketable fruits ($P \leq 0.001$) compared with the Control. The weight of unripe fruits did not change for the three treatments and BER occurred mainly in BigZeo plants (Table 1), however, the incidence of BER was the lowest in CubZeo (5.7%) compared to BigZeo and the Control (9.9%, on average).

The dry matter of commercial fruits was the highest in the Control (exp. 1; $P \leq 0.05$), or in BigZeo (exp. 2; $P \leq 0.01$) (Table 1) and, in both years, the total soluble solid (TSS) content was higher in BigZeo compared to CubZeo treatment ($P \leq 0.001$) (Table 2). The Control plant only exhibited the highest fruit TSS content in the first experiment fruits. Zeolite treatments did not affect the titrable acidity or pH, while BigZeo slightly reduced L* (experiment 1) and improved the hue angle (experiment 2) (Table 2).

3.3. Aerial plant mineral concentration

3.3.1. Leaves and stems

Among the considered mineral elements, only P showed a lower leaf concentration in CubZeo (in both experiments) ($P \leq 0.05$) and BigZeo (in exp. 2) ($P \leq 0.001$) compared with the Control plants (Table 3). Similar changes were also observed in stems (exp. 1, $P \leq 0.001$) (Table 4). In 2021, an improved level of Si was detected in zeolite-treated leaves ($P \leq 0.001$), while sodium leaf concentration was not affected by treatments and the differences in N, K and Mg leaf concentration between treatments were not univocal in the two trials.

In both trials, BigZeo showed the highest stem Si concentration ($P \leq 0.001$, exp.1; $P \leq 0.001$, exp.2), while the stem concentration of the other elements was not (Na), scarcely (K, Mg) or not univocally affected (Ca, N) by the zeolite treatments in the two trials.

3.3.2. Fruits

In both experiments, the phosphorus and nitrogen fruit concentrations were unaffected by treatments, except in the 2022 trial when a reduced level of N occurred in BigZeo ($P \leq 0.01$). On the contrary, the K ($P \leq 0.01$, exp. 1; $P \leq 0.001$, exp. 2), Mg ($P \leq 0.01$, exp. 1; $P \leq 0.01$, exp. 2) and Ca ($P \leq 0.001$, exp. 1; $P \leq 0.05$, exp. 2) concentrations were improved by zeolite treatments and, particularly in exp. 2, that of K was the highest in the BigZeo fruits. The sodium level was higher in the Control compared with BigZeo ($P \leq 0.001$) (exp. 1) or CubZeo ($P \leq 0.001$) (exp.2). Especially in experiment 2 ($P \leq 0.001$), the silicon concentration increased from the Control to CubZeo and BigZeo fruits (Table 5).

Table 2

Quality parameters of fruits of processing tomato plants as affected by foliar application of two zeolite types in 2021 (experiment 1) and 2022 (experiment 2) field trials.

Treatments [‡]	Total soluble solids °Brix	pH	Titrateable acidity (g ⁽¹⁾ /100 mL juice)	L*	hue angle	Chroma
Experiment 1						
BigZeo	5.2 b ⁽²⁾ (±0.1)	4.2 a (±0.01)	0.35 a (±0.02)	67.1 b (±0.4)	49.5 a (±0.4)	49.4 a (±0.5)
CubZeo	4.6c (±0.2)	4.2 a (±0.02)	0.35 a (±0.01)	66.2 b (±0.9)	50.0 a (±0.5)	48.4 a (±0.7)
Control	5.9 a (±0.1)	4.2 a (±0.02)	0.35 a (±0.01)	68.1 a (±0.7)	49.4 a (±0.5)	48.5 a (±0.5)
Significance ⁽³⁾	***	ns	ns	*	ns	ns
Experiment 2						
BigZeo	4.7 a (±0.1)	4.7 a (±0.02)	0.31 a (±0.01)	71.4 a (±0.5)	50.9 b (±1.1)	51.5 a (±0.6)
CubZeo	4.5 b (±0.1)	4.6 a (±0.02)	0.32 a (±0.01)	72.1 a (±0.4)	52.4 a (±0.9)	51.9 a (±0.6)
Control	4.4 b (±0.1)	4.7 a (±0.02)	0.31 a (±0.01)	72.1 a (±0.6)	51.8 ab (±0.9)	52.4 a (±0.7)
Significance ⁽³⁾	***	ns	ns	ns	**	ns

⁽¹⁾ Citric acid monohydrate

⁽²⁾ Different letters within the column indicate significant differences according to the Tukey test ($\alpha = 0.05$).

⁽³⁾ ns, *, **, *** not significant or significant at $P \leq 0.05$, $P \leq 0.01$ and $P \leq 0.001$, respectively

[‡] BigZeo: Micronized zeolite Big-Zeo, Agricola Internazionale, s.r.l.; CubZeo: Cuban zeolite, Bioagrotech s.r.l.

Table 3

Nutrient concentrations in leaves of processing tomato plants as affected by foliar application of two zeolite types in 2021 (experiment 1) and 2022 (experiment 2) field trials.

Treatments [‡]	Na (mg•kg ⁻¹ dry weight)	K	Mg	Ca	P	N	Si
Experiment 1							
BigZeo	2943 a ⁽¹⁾ (±141)	16917 ab (±518)	7729 b (±279)	51492 a (±1443)	1166 a (±40)	2.17 a (±0.08)	1878 a (±101)
CubZeo	3150 a (±140)	17609 a (±791)	8156 b (±219)	52087 a (±1913)	1045 b (±34)	1.94 b (±0.09)	2004 a (±74)
Control	2893 a (±95)	15501 b (±577)	9696 a (±289)	49417 a (±1064)	1168 a (±38)	1.85 b (±0.10)	1633 b (±60)
Significance ⁽²⁾	ns	*	***	ns	*	**	***
Experiment 2							
BigZeo	1531 a (±100)	10273 b (±475)	5105 a (±280)	45951 a (±865)	2305 b (±70)	1.64 b (±0.03)	1600 a (±89)
CubZeo	1751 a (±96)	11498 b (±480)	3024 b (±213)	39309 b (±870)	2232 b (±75)	1.73 b (±0.05)	1622 a (±89)
Control	1559 a (±69)	13609 a (±652)	3189 b (±194)	42731 a (±1042)	2747 a (±97)	2.39 a (±0.09)	1544 a (±33)
Significance ⁽²⁾	ns	***	***	***	***	***	ns

Different letters within the column indicate significant differences according to the Tukey test ($\alpha = 0.05$).

ns, and * ** not significant or significant at $P \leq 0.001$, respectively.

[‡] BigZeo: Micronized zeolite Big-Zeo, Agricola Internazionale, s.r.l.; CubZeo: Cuban zeolite, Bioagrotech s.r.l.

3.4. Leaf physiological status

Leaf gas exchange and fluorescence measured five days after the 4th zeolite application in the 2022 trial are reported in Table 6. Photosynthetic rate (An), stomatal conductance (gs), transpiration rate (E) and photosystem II efficiency (PhiPS2) were lower in CubZeo leaves compared with the other treatments ($P \leq 0.05$). For intercellular CO₂ (Ci), no significant differences emerged between zeolite-treated and Control leaves.

4. Discussion

4.1. Effect of zeolite foliar application on crop growth and productivity

In both experiments, BigZeo foliar application promoted dry biomass accumulation (Fig. 2), despite the growth effectiveness index (gIE_{BZ}) being much higher in 2022 (39.2%) than in 2021 (12.1%). In the 2021 trial, very stressful high temperatures occurred, especially during the

fruit setting (40 to 63 DAT) and maturation periods (74 DAT up to the harvest) (Fig. 1A). Consequently, under this condition a partial counteraction of the positive effect of this zeolite on plant growth may have occurred.

The improved growth in BigZeo plants could be related to the enhanced leaf expansion which was promoted from the early crop stage (Fig. 3A, B). It is well known that leaf area expansion and canopy architecture play a crucial role in determining plant growth by modulating light interception for photosynthesis (Marcelis et al., 1998; Conversa and Elia, 2019; Conversa et al., 2019). Apart from canopy photosynthesis, plant growth may be affected by the photosynthetic capacity at the leaf scale (Albrizio and Steduto, 2003). In this study, no difference in net photosynthesis and photosystem II efficiency between BigZeo and untreated plants was observed, while BigZeo treatment tendentially enhanced the stomatal conductance and the transpiration rate (Table 4). Concerning the application of the Cuban zeolite, results were distinctly affected by the climatic conditions occurring in the two trials. In 2022, when temperatures were within the non-stressing range for a tomato

Table 4

Nutrient concentrations in stems of processing tomato plants as affected by foliar application of two zeolite types in 2021 (experiment 1) and 2022 (experiment 2) field trials.

Treatments [‡]	Na (mg•kg ⁻¹ dry weight)	K	Mg	Ca	P	N	Si
Experiment 1							
BigZeo	3403a ⁽¹⁾ (±172)	22242a (±1060)	5555 a (±247)	28889 a (±1422)	1208 ab (±57)	1.56 a (±0.07)	1837 a (±93)
CubZeo	3249 a (±124)	21986 a (±829)	5345 a (±247)	29450 a (±1535)	1136 b (±35)	1.41 a (±0.07)	1542 b (±60)
Control	3392a (±143)	21244 a (±817)	5635 a (±243)	23574 b (±1060)	1338 a (±43)	1.48 a (±0.08)	1297c (±48)
Significance ⁽²⁾	ns	ns	ns	***	***	ns	***
Experiment 2							
BigZeo	690 a (±35)	12787 a (±501)	571 b (±32)	11943 b (±592)	2135 a (±92)	1.50 b (±0.08)	883 a (±31)
CubZeo	658 a (±33)	8244 b (±331)	788 a (±48)	10682 b (±465)	1917 a (±90)	1.75 b (±0.09)	704 b (±22)
Control	758 a (±36)	12594 a (±669)	707 a (±34)	16670 a (±923)	2102 a (±70)	2.04 a (±0.07)	671 b (±27)
Significance ⁽²⁾	ns	***	**	***	ns	***	***

Different letters within the column indicate significant differences according to the Tukey test ($\alpha = 0.05$).

ns, *, **, *** not significant or significant at $P \leq 0.01$ and $P \leq 0.001$, respectively

[‡] BigZeo: Micronized zeolite Big-Zeo, Agricola Internazionale, s.r.l.; CubZeo: Cuban zeolite, Bioagrotech s.r.l.

Table 5

Nutrient concentrations in fruits of processing tomato plants as affected by foliar application of two zeolite types in 2021 (experiment 1) and 2022 (experiment 2) field trials.

Treatments [‡]	Na (mg•kg ⁻¹ dry weight)	K	Mg	Ca	P	N	Si
Experiment 1							
BigZeo	4857 b ⁽¹⁾ (±218)	50128 a (±2468)	4149 a (±204)	4812 a (±267)	4914 a (±118)	3.13 a (±0.12)	1172 a (±67)
CubZeo	6717 a (±403)	49390 a (± 2804)	4073 a (±176)	5169 a (±225)	4883 a (±240)	3.24 a (± 0.10)	1126 ab (±36)
Control	6157 a (±310)	37583 b (±1668)	3424 b (±150)	3469 b (±137)	4760 a (±198)	3.04 a (±0.10)	1048 b (±21)
Significance ⁽²⁾	***	**	**	***	ns	ns	*
Experiment 2							
BigZeo	1344 a (±58)	30282 a (±893)	1047 ab (±48)	1177 a (±45)	4209 a (±113)	2.03 b (±0.13)	858 a (±13)
CubZeo	1104 b (±34)	28276 b (±786)	1131 a (±51)	1284 a (±65)	4079 a (±96)	2.41 a (±0.14)	822 b (±13)
Control	1259 a (±50)	25967c (±299)	956 b (±43)	997 b (±40)	3954 a (±126)	2.29 a (±0.08)	746c (±13)
Significance ⁽²⁾	***	***	**	*	ns	**	***

Different letters within the column indicate significant differences according to the Tukey test ($\alpha = 0.05$).

ns, *, **, *** not significant or significant at $P \leq 0.05$, $P \leq 0.01$ and $P \leq 0.001$, respectively

[‡] BigZeo: Micronized zeolite Big-Zeo, Agricola Internazionale, s.r.l.; CubZeo: Cuban zeolite, Bioagrotech s.r.l.

Table 6

Leaf gas exchange and chlorophyll fluorescence of processing tomato leaves as affected by foliar application of two zeolite types in 2022 (experiment 2) field trials.

Treatments [‡]	Photosynthetic Rate ($\mu\text{mol m}^{-2} \text{s}^{-1}$ of CO_2)	Stomatal Conductance to H_2O ($\text{mol m}^{-2} \text{s}^{-1}$)	Intercellular [CO_2] ($\mu\text{mol mol}^{-1}$)	Transpiration Rate ($\text{mmol m}^{-2} \text{s}^{-1}$)	PhiPS2
BigZeo	30.3 a ⁽¹⁾ (±1.2)	0.81 a (±0.03)	303.0 a (±2.6)	15.9 a (±0.2)	0.33 a (±0.01)
CubZeo	26.6 b (±1.2)	0.68 b (±0.05)	303.3 a (±2.9)	14.6 b (±0.5)	0.29 b (±0.02)
Control	30.6 a (±0.6)	0.77 ab (±0.06)	296.5 a (±3.3)	15.2 ab (±0.5)	0.33 a (±0.01)
Significance ⁽²⁾	*	*	ns	*	*

⁽¹⁾ Different letters within the column indicate significant differences according to the Tukey test ($\alpha = 0.05$).

⁽²⁾ ns and *, not significant or significant at $p \leq 0.05$, respectively.

[‡] BigZeo: Micronized zeolite Big-Zeo, Agricola Internazionale, s.r.l.; CubZeo: Cuban zeolite, Bioagrotech s.r.l.

crop, the growth was promoted, mirroring the pattern of the BigZeo plants in terms of DM accumulation (Fig. 2 E, F, G, H) and leaf expansion (Fig. 3B). However, a different enhancement of dry biomass between the

two zeolites was highlighted compared with the Control, with the gIECZ being lower in CubZeo than BigZeo plants (21.5% vs 39.2%). Responses of zeolite-treated crops did not seem to be related to the

ecophysiological measurements (Table 4) which underlined that Cuban zeolite application reduced the photosystem II efficiency and the net photosynthesis in particular, even compared with the Control plants.

These preliminary studies suggest that the effect of these zeolites on tomato growth might not be mediated by the photosynthetic machinery, despite an increasing trend in intercellular CO₂ concentration being observed in BigZeo and CubZeo leaves (Ci, Table 4). Similarly, in olive leaves the positive effect of zeolite particle film on CO₂ concentration did not correspond with a photosynthetic rate (An) enhancement (Rotondi et al., 2021).

In 2021, a negative response of crops to Cuban zeolite application was detected with a reduction in dry total biomass accumulation (Fig. 2 A), when compared both with the Control and BigZeo treatments, by 22.0% and 38.9%, respectively. This finding suggests an inhibition effect on the photosynthesis activity by the CubZeo foliar application, however, the photosynthetic parameters were not detected in this part of the experiment. By considering DM partitioning, a decrease in fruit DM accumulation arose in CubZeo plants (65% vs 69.4%, on average) in the 2021 trial, whereas the following year, the application of both zeolites resulted in a higher fruit dry biomass allocation (78%, on average vs 74%), likely supported by a more expanded canopy (Fig. 3B).

In terms of yield, the leaf coating with BigZeo improved marketable production by 36% and fruit organoleptic quality (TSS, Table 2), regardless of the different climatic conditions occurring in the two years, whereas, the particle film with Cuban zeolite was effective (+27% yield) only under non-highly-stressful temperatures. Under less favourable thermal conditions (2021), the marketable yield of CubZeo-treated plants remained similar to that of the Control, despite the difference in fruit DM accumulation (Fig. 2 C). This suggests that the CubZeo coating may have improved the plant water status compared to the Control plants. The latter seem to have experienced a greater temperature/water stress as they showed some well-known related symptoms such as a decrease in fruit water content (highest fruit DM -Table 1- and TSS concentration -Table 2) along with a greater incidence of BER (close to 13%). Averaged over the years, the zeolite particle film reduced the incidence of the BER compared with the Control plants (12%). The effect was more evident with Cuban (5.6%) than BigZeo (9.0%) zeolite type. The occurrence of this physiological disorder in tomato fruits is due to Ca deficiency linked to reduced transpiration flux under temperature/water stress and/or to competition between leaves and fruits that are major sinks for Ca (de Freitas et al., 2011). In this study, in both trials, zeolite leaf coating resulted in a rise in fruit Ca concentration (Table 4), explaining the lower BER occurrence, particularly in CubZeo plants. Physiological adjustments in zeolite-treated plants leading to improved fruit Ca content without affecting the content of this cation in the leaves (Table 3) deserve more in-depth investigation. The transpiration rate could have been affected due to reflective properties suggested for zeolite film particles which in turn reduce leaf temperature. For chabazite zeolite coating, a decrease in light reflectance of olive (Rotondi et al., 2021) or temperature of grapevine (Calzarano et al., 2021) leaves, has been proved. The foliar application of clinoptilolite reduced leaf temperature in apricot and peach (Moale et al., 2021) while a temperature reduction of grapevine berries was observed with a not well-described zeolite (Valentini et al., 2021), however, no data are available for vegetable crops.

The described changes in yield, fruit DM, Ca content and BER occurrence underline differences between zeolites in particle film properties, with CubZeo appearing effective in maintaining water balance in high-temperature stressed plants. On the other hand, these findings do not allow us to explain the best response elicited by the Bigzeo zeolite on plant growth, specifically under heat stress, which makes a substantial difference between the two products. It is likely that changes in their composition (91% clinoptilolite in BigZeo and clinoptilolite: mordenite 70:30 in Cuban zeolite) and in particle shape and/or size, much smaller in BigZeo (size < 6 µm vs < 40 µm, Table A.1), might be responsible for this evidence. Nevertheless, in this study,

neither extensive ecophysiological measurements nor physical characteristics of zeolite film particles were performed, as the main objective was to contribute to filling the gap in the knowledge on the effect of these films on growth in a vegetable crop.

4.2. Effect of zeolite foliar application on plant nutrition

Our hypothesis that zeolite leaf coating may indirectly affect plant nutrient uptake modulating physiological processes was confirmed at least for K, Ca, and Mg. The concentration of these nutrients in fruits, representing 70–80% of the total dry biomass, showed a rise in zeolite-treated plants, especially in the first experiment (+32%, +44%, and +20%, respectively). It seems unlikely that zeolites supply these cations, considering the very low application dose (5 kg ha⁻¹). Moreover, a study dealing with foliar fertilizer added with a clinoptilolite-based zeolite did not show differences in chemical composition compared to the foliar fertilizer without zeolite (Moale et al., 2021). Therefore, more efficient uptake of these cations could be supposed for coated plants, regardless of zeolite type, and the related physiological mechanisms should be investigated along with the reducing effect of zeolites on P accumulation in vegetative parts (Tables 3, 5).

Even if the enhanced cation nutrition may be associated with the general growth promotion of zeolites, it cannot explain the discrepancy between BigZeo- and Cubzeo-treated plants.

As for silicon (Si), it was observed at the highest level in the fruits (Table 5) and stems (Table 4) of BigZeo-treated plants, followed by CubZeo and the Control. Silicon detected in fruits of treated plants can be undoubtedly linkable to the accumulation in tissues as they were carefully washed before sample analysis to remove zeolite residues. Thus, it can be argued that Si was uptaken through leaves and that fruits represent a sink for this element.

Since the bioavailable form of silicon is the soluble mono-silicic acid (H₄SiO₄) (Ma and Yamaji, 2006), its generation in zeolite coating films should be hypothesized, in particular in the case of BigZeo. Soluble Si in the soil is reported to be obtained as a consequence of the chemical weathering of silicate minerals (Constantinescu-Aruxandei et al., 2020), nevertheless, to date no published information is available either on soluble Si production or on Si plant accumulation when zeolites are applied to the canopy.

It is well known that Si is a beneficial element for plants, being involved in many processes to activate plant growth and mitigate biotic and abiotic stresses such as heat stress (Mir et al., 2022).

In several studies reviewed by Laane et al. (2018), foliar sprays with stabilized salicylic acid are reported to increase growth, yield and quality parameters, especially when stress factors are involved. Within the 2021 trial, the foliar application of a Si-based commercial product containing stabilized salicylic acid was also performed (unpublished data) and it resulted in leaf, fruit and stem Si concentrations (1680, 1594 and 950, mg kg⁻¹ DW, respectively) very similar to BigZeo-treated plants. Concurrently, Si- and BigZeo-treated crops showed similar growth and yield. This finding supports the hypothesis that zeolite film particles, especially with the BigZeo type may have supplied leaves with H₄SiO₄. Moreover, the Si accumulation mainly promoted by BigZeo could explain the best crop responses elicited under both stressing and not stressing climatic conditions by this zeolite.

5. Conclusions

To the best of our knowledge, this is the first research dealing with the effects of foliar application of natural zeolites on the growth, productivity and nutrition in a vegetable crop.

It has been proved that irrespective of zeolite type, leaf coatings improve plant K, Mg and Ca nutrition, and the latter has been useful in contrasting the physiological disorder blossom-end-rot.

The main discrepancy between zeolites lies in Si accumulation. The micronized clinoptilolite (BigZeo) particle film enhances at least the

fruit Si content more than Cuban zeolite. Since this element is classed as a biostimulant substance, it can be related to the greater positive effect on the growth and yield of tomato crops exerted by this zeolite. Notably, micronized clinoptilolite is more effective in contrasting high-temperature stress. This characteristic makes using this zeolite extremely interesting in a climate change scenario, where vegetable crops will particularly suffer the increase in intensity and frequency of extreme climate events such as heat waves. Under such conditions, the application of Cuban zeolite appears more questionable since it seems to induce a decrease in dry biomass production. To understand the mechanisms involved in plant responses and effectively exploit foliar spray of zeolites, further comprehensive investigations are needed to define the zeolite film particle characteristics, such as the structural properties of the zeolites, and the associated changes in leaf light reflectiveness, temperature and ecophysiological parameters. Moreover, studies should be addressed to confirm the release of Si soluble species and also to explore the secondary metabolism activation since it is usually related to Si nutrition.

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Appendix

Table A.1

Composition and physical-chemical characteristics of two commercial natural zeolites (Cuban and BigZeo zeolite).

	Unit	Cuban zeolite	BigZeo
Mineralogical composition			
Clinoptilolite	g 100 g ⁻¹	67.5 (± 10)	91 (±1)
Mordenite	g 100 g ⁻¹	32.5 (± 10)	
Cristobalite	g 100 g ⁻¹		4
Mica	g 100 g ⁻¹		2
Plagioclase	g 100 g ⁻¹		1.5 (±0.5)
Chemical composition			
SiO ₂	g 100 g ⁻¹	65.65	80.2
Al ₂ O ₃	g 100 g ⁻¹	11.02	11.8
Na ₂ O	g 100 g ⁻¹	1.07	0.8
K ₂ O	g 100 g ⁻¹	1.74	2.8
CaO	g 100 g ⁻¹	2.68	4.0
MgO	g 100 g ⁻¹	0.93	0.9
Fe ₂ O ₃	g 100 g ⁻¹	1.60	1.3
TiO ₂	g 100 g ⁻¹	0.26	0.2
Si/Al	g 100 g ⁻¹	~ 5	4.8-5.4
Physical-chemical properties			
Particle size	µm	< 40	< 6
Pore size	nm	-	0.4
Specific surface area	m ² g ⁻¹	-	30-60
Cation exchange capacity	mol(+)/kg ⁻¹	1.86	1.90
Specific gravity	g cm ⁻³	2.2	2.3

Table A.2

Significance of the “Year” effect (2021 and 2022) on the analysed characters.

Character	Significance ⁽¹⁾
Marketable fruits (no./plant)	***
Marketable fruits (g/plant)	***
Unripen fruits (no./plant)	ns
Unripen fruits (g/plant)	ns
BER fruits (no./plant)	ns
BER fruits (g/plant)	ns
Fruit dry matter (g kg ⁻¹ FW)	ns
Fruit pH	***
Fruit total soluble solids (°Brix)	ns
Fruit titratable acidity (g/100 mL juice)	***
Fruit - L	***

(continued on next page)

agencies in the public, commercial, or not-for-profit sectors.

CRedit authorship contribution statement

Elia Antonio: Methodology, Supervision, Visualization, Writing – review & editing. **Lazzizzera Corrado:** Investigation. **Bonasia Anna:** Investigation. **Pacifico Salvatore:** Investigation, Resources. **La Rotonda Paolo:** Investigation. **Conversa Giulia:** Conceptualization, Formal analysis, Methodology, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Table A.2 (continued)

Character	Significance ⁽¹⁾
Fruit - h°	***
Fruit - Chroma	***
Fruit-Na (mg•kg ⁻¹ DW)	***
Fruit-K (mg•kg ⁻¹ DW)	***
Fruit-Mg (mg•kg ⁻¹ DW)	***
Fruit-Ca (mg•kg ⁻¹ DW)	***
Fruit-P (mg•kg ⁻¹ DW)	***
Fruit-N (mg•kg ⁻¹ DW)	***
Fruit-Si (mg•kg ⁻¹ DW)	***
Stem-Na (mg•kg ⁻¹ DW)	***
Stem-K (mg•kg ⁻¹ DW)	***
Stem-Mg (mg•kg ⁻¹ DW)	***
Stem-Ca (mg•kg ⁻¹ DW)	***
Stem-P (mg•kg ⁻¹ DW)	***
Stem-N (mg•kg ⁻¹ DW)	***
Stem-Si (mg•kg ⁻¹ DW)	***
Leaf-Na (mg•kg ⁻¹ DW)	***
Leaf-K (mg•kg ⁻¹ DW)	***
Leaf-Mg (mg•kg ⁻¹ DW)	***
Leaf-Ca (mg•kg ⁻¹ DW)	***
Leaf-P (mg•kg ⁻¹ DW)	***
Leaf-N (mg•kg ⁻¹ DW)	ns
Leaf-Si (mg•kg ⁻¹ DW)	***

(1) ns and ***, not significant or significant at $p \leq 0.001$, respectively.

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