

Soil and Plant Nutrition

Comparative study between nutrient-enriched zeolites and conventional fertilizers: effect on kale growth

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ABSTRACT

Synthetic fertilizers have high solubility and when leached through the soil can have environmental and economic impact. Minerals with high cationic exchange capacity, such as zeolites, can reduce nutrient loss. We compared the effect of zeolites enriched with nutrients (NH_4^+ and K^+) and conventional fertilizers on kale growth. Experiments were conducted with 30 pots containing a substrate with: (i) nutrient-enriched zeolites and a phosphate salt (Z-NK+P); (ii) NH_4^+ , K^+ and P salts (NPK); (iii) no additional nutrients (control). After three months, we evaluated kale productivity, absorption of nutrients and nutrient loss on the percolated water. The Z-NK+P and NPK treatments had a higher kale growth and retained more water volume in the first and third month, compared to the control. The NPK treatment released more NH_4^+ (54%) and K^+ (92.9%) in percolated water than the zeolite treatment (15.5% K⁺ and 22.4% NH_4^+) in all the comparisons and had a higher K⁺ concentration in its leaves than control. Both fertilizations were efficient in providing nutrients to the plants; however, zeolites present the advantage by releasing the nutrients gradually, reducing their loss and potentially minimizing environmental and economic impact.

Keywords: productivity; sustainable agriculture; slow-release fertilizer; soil conditioner; zeolite.

INTRODUCTION

In the last 40 years, the Brazilian agricultural sector has grown significantly, especially in grain production, which increased almost fivefold during this period (Embrapa, 2018). One of the causes of this growth is the increased use of agricultural inputs, such as synthetic fertilizers, with consumption increasing from 2 million tons in 1975 to 15 million tons in 2016 in Brazil (Gasques *et al.*, 2018). Among the most used fertilizers are the NPK fertilizers that contain the main nutrients necessary for plant growth, such as nitrogen (N), phosphorus (P), and potassium (K). Despite their important contribution to modern agriculture, the addition of nutrients through synthetic fertilizers is often not efficient, as some types of soil do not have the capacity to retain most of the added nutrients. Sandy soils, for example, have higher permeability (Lepsch, 2011), which can increase the nutrient loss by leaching, especially N and K, because of their high solubility (Lawton *et al.*, 1978).

The loss of nutrients by leaching can, in turn, increase the consumption of fertilizers and the availability of these elements in the soil and water compartments, causing environmental pollution and economic losses to farmers and consumers by increasing the cost of production. These factors can affect countries like Brazil, which, because it does not have important mineral deposits for fertilizer production and produces less than 20% of its demand (SAE/PR, 2020), is the fourth largest consumer of fertilizers (Ibram, 2012).

Nutrients from fertilizers can be retained by active soil solids (clay fraction and humus), mainly in the form of

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cations such as K⁺, Ca²⁺ and NH₄⁺, reducing their loss by leaching (Lepsch, 2011). The presence of some types of minerals can also influence the cation exchange capacity (CEC) of soils (Lopes, 1998). Natural zeolites, for example, can increase nutrient retention in the soil, thus reducing the impact caused using synthetic fertilizers (Bernardi *et al.*, 2010; Nakhli *et al.*, 2017; Soltys *et al.*, 2020; Sun *et al.*, 2020; Jarosz *et al.*, 2022).

Zeolites are hydrated aluminosilicates with a high cation exchange capacity, due to the replacement of some silicon (Si⁴⁺) atoms by aluminum (Al³⁺) in the crystal lattice, whose excess negative charge is compensated by positively charged ions (Na⁺, K⁺, Ca²⁺) that occupy their microporous structure (Barrer, 1982). These cations can be removed and exchanged for others present in the solution/soil (Pabalan & Bertetti, 2001). They also present a high-water retention capacity in free channels and high cationic adsorption capacity, resulting from their large specific surface area, that promotes the retention of nutrients and, consequently, their availability in the soil (Mumpton, 1999; Bernardi et al., 2008). Thus, zeolites have potential use as slow-release fertilizers, delaying the release of nutrients into the soil and making them available for plant absorption, and, consequently, reducing the nutrient loss by leaching.

The use of zeolites in agriculture is as a natural soil conditioner since they can be applied with other materials, such as urea, to increase the availability of nutrients, and thereby the productivity of different crop species (Ando et al., 1996; Baninasab, 2009; Moraetis et al., 2016; Guaya et al., 2020; Medoro et al., 2022). However, some zeolites, especially clinoptilolite, can be naturally loaded with sodium cations (Na⁺) at their exchange sites (Nakhli et al., 2017), and the release of these ions, in excess, into the soil can be toxic to plants, affecting their growth (Dias & Blanco, 2010). Thus, the direct application of zeolites should be carried out with caution, especially in soils in arid and semi-arid regions that already have high levels of Na⁺ (Dias & Blanco, 2010). One way to minimize this potential problem is to replace the Na⁺ present in the mineral structure with other ions of interest, such as K^+ and NH_4^+ , through treatments to saturate natural zeolites before soil application. Some studies have also demonstrated the high selectivity of clinoptilolite for K^+ and NH_4^+ ions (Ames Junior, 1960; Manikandan & Subramanian, 2014; Shinzato et al., 2020).

Although the potential use of zeolites as a slow nutrient release agent has been studied (Mumpton, 1999; Kavoosi, 2007; Aghaalikhani *et al.*, 2012; Li *et al.*, 2013a; 2013b), there is still limited information about the effects of the use of zeolites modified with K^+ and NH_4^+ cations on plant productivity and nutrients releasing mechanism. Therefore, the main contribution of this study was to investigate the use of nutrient-enriched zeolites and compare their efficiency with commercial fertilizers, under tropical climate conditions and in nutrient-poor substrates.

MATERIAL AND METHODS

Preparation of modified zeolites

The samples of natural zeolites used were from the Tasajeras-Piojillo (Cuba) deposits, supplied by the industry Celta Brasil. These samples have a granulometry of 0.4 to 1.0 mm and are constituted by clinoptilolite (98%) and mordenite (2%) and present a CEC of 1.30 meq g⁻¹.

To prepare the K⁺-modified zeolites, 700 g of this adsorbent was added to 1 L of 1 mol L⁻¹ KCl solution (Sigma-Aldrich). In the preparation of the zeolites with NH₄⁺, 700 g of zeolite were added to 1 L of 1 mol L⁻¹ of NH₄Cl (Sigma-Aldrich). These mixtures were agitated for 24 h in a Wagner-type shaker at 25 °C, filtered and washed with distilled water until the absence of Cl⁻, tested with a HgNO₃ solution (Sigma-Aldrich). The sample was dried at 80 °C for 48 h. Previous tests performed on these zeolites modified with K⁺ and NH₄⁺ revealed that they adsorbed 21 mg K⁺ and 14 mg NH₄⁺ per gram of sample. These samples were used in the kale cultivation experiments.

Kale growing experiment

The experiment was conducted in the city of São Paulo (SP-Brazil) in an open area of 420 x 200 cm, thus being subject to the environmental conditions of the region. According to Koeppen's classification, the predominant climate of São Paulo is Cwa (humid subtropical climate), which has hot and humid summers (December, January and February), with temperatures above 22 °C, and cold and dry winters (June, July and August), with temperatures below 18 °C (Embrapa, 2023; EMIAG/USP, 2023). In general, the entire region of the state presents total monthly precipitation values between 180 mm and 340 mm in the summer period (INPE, 2023). Specifically, during the experiment (which took place from June to September) the total rainfall of the region was 97.8 mm and the average temperature was 16.5 °C, whose maximum and minimum averages were, respectively, 22.1 °C and 15 °C (INMET, 2021). We

chose kale (*Brassica oleracea* L.) as a model species for this experiment because it can easily be cultivated at any time of the year and develops rapidly (about four months). Thus, in April 2021, kale seedlings were produced from seeds (ISLA Sementes brand). About 70 kale seeds were planted in pots containing a substrate prepared with 1 kg of vegetable soil mixed with 11.25 g of conventional chemical fertilizer NPK (Dimy – Mixed Mineral Fertilizer, 10:10:10). After germination and initial kale growth (41 days), in June 2021, 30 seedlings (10 to 15 cm in height and at least 4 to 5 leaves) were transferred to the cylindrical experiment pots (17 cm high and 15 cm diameter), with one seedling per pot.

To provide good porosity and permeability, the base of each pot was filled with 1 kg of fine sand, and on top of this layer, another 1 kg of a mixture prepared with 50% fine sand and 50% topsoil was added. The mixture of sand with topsoil was prepared to use a substrate relatively poor in nutrients, but sufficient to produce plant growth without the addition of fertilizer (control). In this way, the observation of the effect of fertilizer addition on plant growth could be studied. The characterization of this soil (Table 1) was carried out at the Laboratório de Análises Químicas do Solo of the Escola Superior de Agricultura Luiz de Queiroz (ESALQ)/Universidade de São Paulo -USP, using the following methods: pH in water; calcium (Ca) and magnesium (Mg) by extraction with 1 mol L^{-1} potassium chloride and determination in an atomic absorption spectrophotometer; aluminum (Al) by extraction with 1 mol L⁻¹ KCl and determination by titrimetry; potassium (K) by extraction with Mehlich 1 and determination in a flame photometer; phosphorus (P) by extraction with Mehlich 1 and determination by colorimetry (Teixeira et al. 2017); potential acidity (H+Al) by extraction with calcium acetate and determination by titrimetry; organic matter (OM) by titration (Camargo et al. 2009). Since NH_{4}^{+} ions were weakly bound on the soil surface, they were determined by the cation exchange method (Costa et al., 2018) using 1 mol L⁻¹ KCl; then the NH_{4}^{+} concentration was determined by the Nessler method on the HI83215

Table 1: Chemical characterization of the soil

spectrophotometer (HANNA Instruments).

For this experiment, three series of treatments with 10 pots for each treatment, were prepared:

(1) Z-NK+P: 36 g of NH_4^+ -zeolite and 24 g of K⁺-zeolite, and 1 g of dipotassium phosphate (K_2HPO_4 , Sigma-Aldrich) were added to the mixed soil layer;

(2) NPK: 1.6 g NH₄Cl, 1 g KCl and 1 g of K_2 HPO₄ were added to the mixed soil layer;

(3) Control: substrate with no fertilizer.

The amount of salts (NPK) and modified zeolites used in the NPK and Z-NK+P treatments were determined based on the recommendation of the conventional NPK product (with 10% of N, P and K), where 10 g of this fertilizer is mixed with 2 kg of soil. Therefore, 10 g of conventional chemical fertilizer has approximately 1 g of each nutrient in 2 kg of soil, or 0.5 g of each nutrient for 1 kg of soil. Likewise, the amount of zeolite added to the Z-NK+P experiment was based on the amount of these ions present in each gram of mineral (determined previously). Despite contributing extra K⁺ (about 0.11 g), K₂HPO₄ salt was added in the same amount in the two treatments with fertilizer to provide phosphorus to the plants.

After transplanting the kale seedlings to the experimental pots, they were irrigated daily with tap water (150 mL) for 26 days, except on rainy days. Then, the plants were irrigated on alternate days using 100 mL of water, until the end of the experiment. The volume of water retained in soil was calculated from the difference between the irrigation volume and the percolated volume (collected from the pots).

Percolated water analysis

During the first month, the percolated water accumulated in plastic containers placed under each pot was collect every 10 days. These solutions were filtered and preserved with 10% HCl until the determination of K^+ and NH_4^+ concentrations. From the second month on, the percolated water was collected every 20 days, totaling six collections until the end of the experiment. The volume and pH of each percolated water sample was determined during the

рН	ОМ	Р	K	Ca	Mg	Al	\mathbf{NH}_{4}^{+}	EB	H+Al	CEC	BS	m
	(mg kg ⁻¹)						(mmolc kg ⁻¹)			(%)		
6.01	17800	11	68.8	810	123.9	< 0.1	28.3	27.1	27.6	54.7	50	0

 $EB = sum \ of \ exchange able \ bases; \ CEC = cation \ exchange \ capacity; \ BS = CEC \ base \ saturation; \ m = aluminum \ saturation.$

experiment using a glass volumetric burette and a pH meter (HI2221/Hanna Instruments), respectively.

The concentration of NH_4^+ leached by the percolating water was determined by the same method described in the previous section ("Kale growing experiment"), while K⁺ levels were analyzed using flame photometry (DM-62/Digimed).

Kale productivity

To evaluate the effect of the type of fertilizer used on kale growth, the height, number of leaves and final biomass of each plant was recorded. The plant height was measured from its base near the level of the substrate, using a graduated ruler, and the number of leaves was counted. Both measurements were recorded at 30, 60 and 90 days after transplanting the seedlings. For the evaluation of kale growth, the difference between the initial values (determined at the time of kale transplanting) and later one (one, two and three months after transplanting) was calculated for height and the number of leaves.

After three months the experiment was ended (September 11, 2021). Then, the kale biomass of each pot was collected to evaluate plant development, shoots (stems and leaves) and roots. For this determination, the plants were dried in an oven at 70 °C to constant weight and the shoots were separated from the roots before weighing (+/- 0.001 g). At the end of the experiment, the nutritional concentration of the kale leaves was evaluated by the concentration of K⁺. The NH₄⁺ ions were not determined as they are incorporated into the structures of amino acids and plant metabolites (Batista et al., 2018). To extract K⁺ from the plant, 0.5 g of kale leaves were washed and dried in an oven at 60 °C for 48 hours and treated with 10 mL of H₂SO₄ and 4.5 mL of H₂O₂, according to the method proposed by Li et al. (2013a). After centrifugation/filtration, the K⁺ concentration of each sample was determined using a flame spectrophotometer.

Statistical analysis

To evaluate the effect of each type of fertilizer on the kale parameters (vertical growth, number of leaves, final biomass, volume of water retained in the soil, pH, concentration of NH_4^+ and K^+ in the percolated water and K^+ concentration in kale leaves), all the results were subjected to a one-way analysis of variance (ANOVA) with 5% significance level. For each of the response variables, the type of fertilizer (Z-NK+P, NPK or control) was used as

the predictor variable. In addition, the Tukey test was used for the comparison between groups, and visual graphical analyses were used to verify that the ANOVA premise of homogeneity of variances was met.

RESULTS AND DISCUSSION

Percolated water analysis

After the first 10 days of the experiment, the pots under Z-NK+P treatment showed around 31% higher water retention when compared to the control ($F_{2,27} = 4.34$; p = 0.023; Figure 1a). During this period, the average percentage of water retained in the Z-NK+P, NPK and control treatments were 50%, 47% and 38%, respectively.

In the third month of the experiment, with the accumulated volume of 20 days, both the Z-NK+P and NPK treatments showed a significant difference in relation to the control ($F_{2,27} = 11.84$; p = 0.0002), presenting on average a 36% higher water retention when compared to the control (Figure 1b). On average, 75% of the water used for irrigation was retained in Z-NK+P, 72% in NPK and 54% in the control.

Both treatments with fertilizers retained more irrigation water than the control experiment. A possible explanation for this result is that kale growth in these two treatments (Z-NK+P and NPK) was higher than in the control (see results below). During growth, plants demand more water to maintain their physiological processes. Thus, it is possible that the kale under the Z-NK+P and NPK treatments, absorbed more water than those from control. Another possibility is related to the ability of zeolites to retain water in their channels, resulting in a greater water retention at the beginning of the experiment, when the plants were still small, and therefore had less influence on the results.

Regarding the concentrations of K⁺ and NH₄⁺ found in the percolated water, over the three months of the experiment, the NPK treatment was, in general, responsible for the greatest release of these nutrients into the percolated water (Figure 2a and 2b; in all temporal comparisons p < 0.0001). When the K⁺ data is observed (Figure 2a), we noticed that at the beginning of cultivation the NPK treatment presented a significant and very relevant difference when compared to the other two treatments (Z-NK+P and control), which do not present a significant difference between them. Over time, the release of K⁺ from the NPK treatment decreased considerably, while Z-NK+P and the



Figure 1: Mean and standard error of the volume of water retained in the three treatments after (a) 10 days from the beginning of the experiment, with an accumulated volume of 10 days, and (b) after 90 days of the experiment, with an accumulated volume of 20 days. Different letters at the outer end of the bars represent significantly different means, according to Tukey's test (n = 10).

control presented a constant release (Figure 2a). At the end of the experiment, the Z-NK+P and NPK treatments no longer showed a significant difference between them, with only a difference from the control treatment compared to the other two (Z-NK+P and NPK) being observed. For NH_4^+ concentrations (Figure 2b) a similar scenario to that of K⁺ release was observed, and in this case, at the end of the experiment, only the Z-NK+P treatment showed a significant difference when compared to the other two treatments (NPK and control).

In general, the NPK treatment lost significant amounts of K^+ and NH_4^+ through leaching. In zeolites, these nutrients are adsorbed in the micropores, and their release occurs gradually by ion exchange, consequently, their losses are reduced (Mumpton, 1999; Bernardi *et al.*, 2008; Wu *et al.*, 2013). Furthermore, even after the adsorbed nutrients are depleted, zeolites will continue to perform ionic exchange and adsorb any new nutrients added to the soil. Thus, in addition to mitigating the potential environmental impact resulting from nutrient loss, the use of zeolites can also reduce economic expenses, as they can be replenished by adding nutrients to the soil, either for a new planting or for plants with long growing cycles.

Eslami *et al.* (2018) also observed that zeolites modified with NH_4^+ and K^+ are able to release these nutrients in a controlled manner, reducing leaching losses in sandy soils with low organic matter concentration. Although the nutrients from the NPK treatments were continuously leached, the three- month period of this experiment was not enough to fully deplete them. After three months 15.5% K^+ and 22.4% NH_4^+ were lost by leaching in the Z-NK+P treatments, while the loss of these nutrients in the NPK treatment was considerably higher: 92.9% K^+ and 54% NH_4^+ . The lower NH_4^+ loss in relation to K^+ in the NPK treatments may be related to the nitrification of ammonium to nitrite/nitrate, however these anions were not analyzed in this study.

Regarding the pH of the percolated water, in the first 10 days of the experiment, no difference was found between the means of the three treatments (Figure 3a). This result indicates that the fertilization treatment had no impact on pH during this period ($F_{2,27} = 0.56$; p = 0.58). However, after 70 days, a reduction in pH (from 6 to 5) was observed in the percolated water from treatments Z-NK+P and NPK, and this pH value remained stable until the end of the experiment (Figure 3b). The decrease of pH can be explained by the fact that ammonia nitrogen, present in systems with fertilization (Z-NK+P and NPK), can acidify the soil after being absorbed by the plants roots or when undergoing biological oxidation during the nitrification process (Borges &



Figure 2: Mean and standard error of the concentration of leached (a) potassium and (b) ammonium in the percolated water collected from the three treatments during the three months of the experiment. Different letters at the outer end of the bars represent significantly different means, according to Tukey's test (n = 10), for that collection period.



Figure 3: Mean and standard error of pH of the leachate samples of the three treatments after (a) 10 and (b) 90 days from the beginning of the experiment. Different letters at the outer end of the bars represent significantly different means, according to Tukey's test (n = 10).

Silva, 2011). Shinzato *et al.* (2020) also verified a decrease in the soil pH (from 6.5 to 5.5) after 20 days of incubation of soil samples with zeolites loaded with NH_4^+ due to the nitrification process.

Although soil pH is a determining factor for the availability of nutrients to plants (Da Silva, 2020), soil acidification is a natural process that can be accelerated with the insertion of nitrogen fertilizers (Ciotta *et al.*, 2002), especially those produced with ammonium sulfate, which have the highest soil acidification capacity (acidity index 110) (Isherwood, 2000; Melém Júnior *et al.*, 2001; Merten *et al.*, 2019). In this context, the pH reduction found in this study was an expected reaction, and no differences were observed between the types of fertilizers used. In addition, this pH variation was of low magnitude and apparently did not affect kale development.

In summary, we observed a strong influence of the addition of external nutrients on water retention, pH and level of leached nutrients (NH_4^+ and K^+) in the percolated water.

Kale productivity

Although the type of fertilizer adopted affected kale vertical growth both in the first and third months ($F_{2,27} = 10.65$; p = 0.0004 and $F_{2,27} = 32.17$; p < 0.0001, respectively), the Z-NK+P and NPK treatments did not present significant differences between them (Figure 4). On the

(a)

other hand, a significant difference was found between the two fertilization treatments and the control (Figure 4). This result was also found in the second month of cultivation ($F_{2,27} = 34.92$; p < 0.0001). The kale with external sources of nutrients (Z-NK+P and NPK) grew 4.6 times faster in the first month (Figure 4a) and 3.9 times more in the third month (Figure 4b), when compared to the control. On average, there was an increase in vertical growth of approximately 35% for Z-NK+P, 32% for NPK and 7% for the control in the first month after transplantation. In the third month, this increase was 123% for Z-NK+P, 103% for NPK and only 29% for the control.

Regarding the increase in the number of plant leaves in the first month, we also observed a significant difference between the control and fertilization treatments (Z-NK+P and NPK) ($F_{2.27} = 21.71$; p < 0.0001), an increase of 4 times (Figure 5a). During the second month, this scenario changed, with a significant difference found only between the NPK-treated kale and the control ($F_{2.27} = 4.85$; p =0.016), with an increase of 73% (Figure 5b). Thus, after two months of the experiment, no significant differences were found in the increase in the number of leaves in the Z-NK+P treatment compared to the control (Figure 5b). In the third month, no difference was identified between the three treatments ($F_{2.27} = 1.92$; p = 0.17), suggesting that after three months the type of fertilization did not influence

■Z-NK+P ■NPK ■Control **Figure 4**: Mean and standard error of the difference in height of kales in the three treatments after (a) one and (b) three months of the experiment. Different letters at the outer end of the bars represent significantly different means, according to Tukey's test (n = 10).





Figure 5: Mean and standard error of the increase in the number of kale leaves in the three treatments after (a) one, (b) two and (c) three months of the experiment. Different letters at the outer end of the bars represent significantly different means, according to Tukey's test (n = 10).

the increase in the number of leaves (Figure 5c).

The kale final biomass, analyzed by means of the data on root development, indicates that there was no difference between the fertilization treatments (Figure 6a; $F_{2,27} =$ 0.001 and p = 0.999). The shoot biomass of the Z-NK+P and NPK treatments showed no significant differences between them, however, these two treatments were an average 5.5 times higher than the control ($F_{2,27} = 12.24$; p = 0.0002; Figure 6b).

About the nutritional quality of the kales, observed through the K⁺ concentration in the leaves, there was only a significant difference between the NPK and the control treatment (Figure 7; $F_{2,17} = 3.35$ and p = 0.059). NPK kale leaves had, on average, a K⁺ concentration 1.5 times higher (Figure 7).

As expected, the results of this experiment show that

the addition of external sources of nutrients (Z-NK+P and NPK treatments) has a strong positive effect on growth and shoot biomass in kale. However, we found no significant difference between the Z-NK+P and NPK treatments over the three-month experiment, both in terms of productivity and nutritional quality.

As conventional fertilization makes nutrients available to plants more quickly (Ronquim, 2010), the NPK treatment showed higher K⁺ levels in the kale leaves than the control treatment. However, the property of zeolites in retaining and gradually releasing nutrients into the soil was able to meet the nutritional needs of the plants similarly to the conventional treatment (NPK), as well as guaranteeing their availability for a longer period (Mumpton, 1999; Polat *et al.*, 2004; Reháková *et al.*, 2004; Bernardi *et al.*, 2008). Torma *et al.* (2014) analyzed the influence of



Figure 6: Mean and standard error of kale biomass, in the three treatments in (a) root and (b) shoot at the end of the three months of the experiment. Different letters at the outer end of the bars represent significantly different means, according to Tukey's test (n = 10).

a natural zeolite on the dynamics of mineral nitrogen in the soil and observed the gradual release of nutrients by the mineral. According to the authors, after one month of zeolite application, the surface layer of the soil contained 14% to 20% more $\rm NH_4^+$ (depending on the amount of zeolite applied) than the control system. Three months later, it was observed that the amount $\rm NH_4^+$ present in the system with zeolite increased from 24% to 59%, and in the fifth month of the experiment the zeolite treatment contained 68.5 to 86.9 mg kg⁻¹ of $\rm NH_4^+$ in the soil, while the control presented only 55.2 mg kg⁻¹ (Torma *et al.*, 2014).

In addition, some studies show that zeolites have a positive effect on the productivity of different crop species, such as apple, rice, sunflower, wheat, and canola (Mumpton, 1999; Kavoosi, 2007; Aghaalikhani *et al.*, 2012; Guaya *et al.*, 2020). For example, in the study carried out with sunflowers (*Helianthus annuus*), an increase in the biomass of the cultivated plants was observed with zeolites enriched in NH_4^+ and PO_4^{3-} , in both in clayey and sandy soils, as well as an increase in the levels of these nutrients in the plant tissues (Guaya *et al.*, 2020). Furthermore, the authors also found that, after the experimental period, both soils



Figure 7: Mean and standard error of the potassium concentration in the tissue of kale leaves, in the three treatments, at the end of the three-month experiment. Different letters at the outer end of the bars represent significantly different means, according to Tukey's test (NPK and Z-NK+P n = 8; Control n = 4).



Figure 8: Schematic summary of the main results found in this study.

contained a reserve of NH_4^+ , NO_3^{-1} and PO_4^{3-} sufficient for a second crop growth cycle. Results of a study carried out with another kale species *Brassica alboglabra* Bailey (different from the one used in this study), revealed that after 18 weeks kale grown with NH_4^+ and K^+ loaded zeolites showed 5% more biomass, as well as significantly higher levels of nutrients (Na, Mg and K), than kale grown with conventional fertilizer (Li *et al.*, 2013a). In this context, Eghtedary-Naeini *et al.* (2016) also showed that the addition of zeolites enriched by essential cations and iron in soilless cucumber culture increased plants yield and vigor.

Although the results of this kind of study can vary according to the crop species and methodology applied, the time taken to conduct the experiment is a very important parameter to consider. In our study, the cultivation time lasted three months, while the previously mentioned studies lasted between four and eight months. Therefore, if we had extended the period of our experiment, until nutrient depletion in the NPK treatment, the difference in the growth and nutritional concentration of kale between the treatments would probably have been more pronounced. Aainaa et al. (2018) also observed similar results in treatments conducted with clinoptilolite + 75% of the recommended NPK dose, compared to the full dose of NPK, in maize grown in acidic soil. For the authors, just two crop cycles were not enough to observe the real effects of applying zeolite to the soil.

CONCLUSIONS

The addition of external nutrient sources on kale growth improved shoot biomass development. However, over

time, the NPK fertilizer source lost more nutrients through leaching than the zeolite-bearing fertilizers. Although the release of nutrients from the zeolite-bearing fertilizers was gradual and continuous, it was sufficient to unrestricted plant growth, as well as for adequate assimilation of K^+ , when compared to the NPK treatment. Zeolite also improved water retention during kale growth. Figure 8 shows the main results found in this study. In this context, our results indicates that the use of zeolites as slow-release fertilizers seems feasible because it provides enough nutrients for kale growth and prevents the loss of nutrients through the soil. Given the economic importance of the agricultural sector in Brazil, our study highlights the advantages of using mineral-based slow-release fertilizers to reduce costs and preserve the environment.

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The authors declare no competing interests.

REFERENCES

Aainaa HN, Ahmed OH & Majid NMAB (2018) Effects of clinoptilolite zeolite on phosphorus dynamics and yield of Zea Mays L. cultivated on an acid soil. PLoS One, 13:e0204401.

Aghaalikhani M, Gholamhoseini M, Dolatabadian A, Khodaei-Joghan A & Asilan KS (2012) Zeolite influences on nitrate leaching, nitrogen-use efficiency, yield and yield components of canola in sandy soil. Archives of Agronomy and Soil Science, 58:1149-1169.

Ames Junior LL (1960) The cation sieve properties of clinoptilolite.

American Mineralogist: Journal of Earth and Planetary Materials, 45:689-700.

- Ando H, Mihara C, Kakuda K & Wada G (1996) The fate of ammonium nitrogen applied to flooded rice as affected by zeolite addition. Soil Science and Plant Nutrition, 42:531-538.
- Baninasab B (2009) Effects of the application of natural zeolite on the growth and nutrient status of radish (*Raphanus sativus L*.). The Journal of Horticultural Science and Biotechnology, 84:13-16.
- Barrer RM (1982) Hydrothermal Chemistry of Zeolites. London, Academic Press. 360p.
- Batista MA, Inoue TT, Esper Neto M & Muniz AS (2018) Princípios de fertilidade do solo, adubação e nutrição mineral. In: Brandão Filho JUT, Freitas PSL & Goto R (Eds.) Hortaliças-fruto. Maringá, EDUEM. 113-162p.
- Bernardi ACC, Monte MBM, Paiva PRP, Werneck CG, Haim PG & Polidoro JC (2008) Potencial do uso de zeólitas na agropecuária. São Carlos, Embrapa Pecuária Sudeste. 46p.
- Bernardi ACC, Monte MBM, Paiva PRP, Werneck CG, Haim PG & Barros FS (2010) Dry matter production and nutrient accumulation after successive crops of lettuce, tomato, rice, and andropogongrass in a substrate with zeolite. Revista Brasileira de Ciência do Solo, 34:435-442.
- Borges AL & Silva DJ (2011) Fertilizantes para fertirrigação. In: Sousa VF, Marouelli WA, Coelho EF, Pinto JM & Coelho Filho MA (Eds.) Irrigação e fertirrigação em fruteiras e hortaliças. Brasília, Embrapa Informação Tecnológica. 253-264p.
- Ciotta MN, Bayer C, Ernani PR, Fontoura SMV, Albuquerque JA & Wobeto C (2002) Acidificação de um Latossolo sob plantio. Revista Brasileira de Ciência do Solo, 26:1055-1064.
- Costa CL, Braz CEM, Kamogawa MY, Bernardi ACC, Souza GB & Nogueira ARA (2018) Determinação de nitrato e amônio por sistema de análise em fluxo em amostras de lixiviado de solo. São Carlos, Embrapa Pecuária Sudeste. 18p. (Circular Técnica, 80).
- Da Silva J (2002) Adubação e nutrição. Available at: https://www.agencia.cnptia.embrapa.br/gestor/pimenta/arvore/CONT000gn0k9bx-a02wx5ok0liq1mqs8yoptq.html- Accessed on: July 20th, 2022.
- Camargo OA, Moniz AC, Jorge JA & Valadares JMAS (2009) Métodos de Análise Química, Mineralógica e Física de Solos do Instituto Agronômico de Campinas. Campinas, Instituto Agronômico. 77p. (Boletim técnico, 106).
- Dias NS & Blanco FF (2010) Efeitos dos sais no solo e na planta. In: Gheyi HR, Dias NS & Lacerda CF (Eds.) Manejo da salinidade na agricultura: estudos básicos e aplicados. Fortaleza, INCTSal. 86-88p.
- Embrapa Empresa Brasileira de Pesquisa Agropecuária (2018) Visão 2030: O futuro da agricultura brasileira. Brasília, Embrapa. 212p.
- Embrapa Empresa Brasileira de Pesquisa Agropecuária (2023) Clima. Available at: <https://www.cnpf.embrapa.br/pesquisa/efb/clima.htm>. Accessed on: May 19th, 2023.
- EMIAG-USP Estação Meteorológica do Instituto de Astronomia, Geofísica e Ciências Atmosféricas da Universidade de São Paulo (2023) Informações sobre as Estações do Ano na Cidade de São Paulo. Available at: http://www.estacao.iag.usp.br/seasons/index.php Accessed on: May 19th, 2023.
- Eghtedary-Naeini A, Gobaldi M & Hoodaji M (2016) Using enriched zeolite as a slow release iron fertilizer for soilless greenhouse cultivation of cucumber. Journal of Plant Nutrition, 39:523-530.
- Eslami M, Khorassani R, Coltorti M, Malferrari D, Faccini B, Ferretti G, Giuseppe D, Fotovat A & Halajnia A (2018) Leaching behaviour of a sandy soil amended with natural and NH_4^+ and K^+ saturated clinoptilolite and chabazite. Archives of Agronomy and Soil Science, 64:1142-1151.
- Gasques JG, Bacchi MRP & Bastos ET (2018) Crescimento e Produtividade da Agricultura Brasileira de 1975 a 2016. Brasília, Ipea. 9p. (Carta de Conjuntura, 38).
- Guaya D, Mendoza A, Valderrama C, Farran A, Sauras-Yera T & Cortina JL (2020) Use of nutrient-enriched zeolite (NEZ) from urban waste-

waters in amended soils: Evaluation of plant availability of mineral elements. Science of the total environment, 727:138646.

- IBRAM Instituto Brasileiro de Mineração (2012) Information and Analysis of the Brazilian Mineral Economy. 7^a ed. Brasília, IBRAM. 68p.
- INMET Instituto Nacional de Meteorologia (2021) Tabela de dados das estações. Available at: https://tempo.inmet.gov.br/TabelaEstacoes/A001>. Accessed on: May 19th, 2023.
- INPE Instituto Nacional de Pesquisas Espaciais (2023) Vulnerabilidade das megacidades brasileiras às mudanças climáticas. Available at: http://megacidades.ccst.inpe.br/sao_paulo/VRMSP/capitulo3. php>. Accessed on: May 19th, 2023.
- Isherwood KE (2000) Mineral Fertilizer Use and the Environment. Paris, International Fertilizer Industry Association. 53p.
- Jarosz R, Szerement J, Gondek K & Mierzwa-Hersztek M (2022) The use of zeolites as an addition to fertilisers - A review. Catena, 213:106125.
- Kavoosi M (2007) Effects of zeolite application on rice yield, nitrogen recovery, and nitrogen use efficiency. Communications in soil science and plant analysis, 38:69-76.
- Lawton K, Coelho MA & Crisóstomo LA (1978) Movimento e perdas por lixiviação de nutrientes solúveis aplicados a solos do Estado do Ceará, Brasil. Ciência Agronômica, 8:09-18.
- Lepsch IF (2011) 19 Lições de Pedologia. São Paulo, Oficina de textos. 456p.
- Li J, Wee C & Sohn B (2013a) Effect of ammonium-and potassium-loaded zeolite on kale (Brassica alboglabra) growth and soil property. American Journal of Plant Sciences, 4:1976-1982.
- Li Z, Zhang Y & Li Y (2013b) Zeolite as slow release fertilizer on spinach yields and quality in a greenhouse test. Journal of Plant Nutrition, 36:1496-1505.
- Lopes AS (1998) Manual internacional de fertilidade do solo. Piracicaba, Potafos. 186p.
- Manikandan A & Subramanian KS (2014) Fabrication and characterization of nanoporous zeolite based N fertilizer. African Journal of Agricultural Research, 9:276-284.
- Medoro V, Ferretti G, Galamini G, Rotondi A, Morrone L, Faccini B & Coltorti M (2022) Reducing Nitrogen Fertilization in Olive Growing by the use of natural chabazite-zeolite as soil improver. Land, 11:1471.
- Melém Júnior NJ, Mazza JA, Dias CTS & Briske EG (2001) Efeito de fertilizantes nitrogenados na acidificação de um Argissolo Vermelho Amarelo Latossólico Distrófico cultivado com milho. Embrapa Amapá, 2:75-89.
- Merten GM, Patel M & Richart A (2019) Potencial acidificante de diferentes fertilizantes fosfatados aplicados em dois solos do Paraná. Revista Cultivando o Saber, 12:32-42.
- Moraetis D, Papagiannidoub S, Pratikakisb A, Pentarib D & Komnitsas K (2016) Effect of zeolite application on potassium release in sandy soils amended with municipal compost. Desalination and Water Treatment, 57:13273-13284.
- Mumpton FA (1999) La roca magica: uses of natural zeolites in agriculture and industry. Proceedings of the National Academy of Sciences, 96:3463-3470.
- Nakhli SAA, Delkash M, Bakhshayesh BE & Kazemian H (2017) Application of zeolites for sustainable agriculture: a review on water and nutrient retention. Water, Air, & Soil Pollution, 228:464.
- Pabalan RT & Bertetti FP (2001) Cation-exchange properties of natural zeolites. Reviews in mineralogy and geochemistry, 45:453-518.
- Polat E, Karaca M, Demir H & Onus AN (2004) Use of natural zeolite (clinoptilolite) in agriculture. Journal of fruit and ornamental plant research, 12:183-189.
- Reháková M, Cuvanová S, Dzivák M, Rimár J & Gaval'ová Z (2004) Agricultural and agrochemical uses of natural zeolite of the clinoptilolite type. Current Opinion in Solid State and Materials Science,

8:397-404.

- Ronquim CC (2010) Conceitos de fertilidade do solo e manejo adequado para as regiões Tropicais. Campinas, Embrapa Territorial. 34p. (Boletim de Pesquisa e Desenvolvimento, 8)
- SAE- Secretaria Especial de Assuntos Estratégicos (2020) Produção Nacional de Fertilizantes. Available at: https://www.gov.br/planalto/ptbr/assuntos/assuntos-estrategicos/documentos/estudos-estrategicos/ sae_publicacao_fertilizantes_v10.pdf, 2020>. Accessed on: February 20th, 2022.
- Soltys LM, Mironyuk IF, Tatarchuk TR & Tsinurchyn VI (2020) Zeolite-based composites as slow release fertilizers (Review). Physics and Chemistry of Solid State, 21:89-104.
- Sun Y, He Z, Wu Q, Zheng J, Li Y, Wang Y, Chen T & Chi D (2020) Zeolite amendment enhances rice production, nitrogen accumulation and translocation in wetting and drying irrigation paddy field. Agricultural Water Management, 235:106126.
- Shinzato MC, Wu LF, Mariano TO, Freitas JG & Martins TS (2020) Mineral sorbents for ammonium recycling from industry to agriculture. Environmental Science and Pollution Research, 27:13599-13616.
- Teixeira PC, Donagemma GK, Fontana A & Teixeira WG (2017) Manual de métodos de análise de solo. Brasília, Embrapa. 574p.
- Torma S, Vilcek J, Adamisin P, Huttmanova E & Hronec O (2014) Influence of natural zeolite on nitrogen dynamics in soil. Turkish Journal of Agriculture and Forestry, 38:739-744.
- Wu LF, Shinzato MC, Andrade S, Franchi JG & Andrade VS (2013) Efeito da adição de zeólita e vermiculita na lixiviação de potássio do solo. Revista do Instituto Geológico, 34:57-67.