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Nitrogen, Potassium, and Nitrate Concentrations of Lettuce Grown in a Substrate with KNO_3-Enriched Zeolite

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Zeolite minerals improve the efficiency of nutrient use by plants by helping to regulate the release of nitrogen and nitrate accumulation in tissues. The main objectives of this research were to evaluate effects of the addition of zeolite enriched with potassium nitrate (KNO_3) on the nitrate (NO_3-N) and potassium (K) levels of lettuce shoot. Treatments arranged in a completely randomized block design with three replications comprised two types of the natural zeolite: concentrated zeolite, zeolite + KNO_3, and a control grown in substrate fertilized with a nutrient solution without zeolite supply. Four levels of enriched zeolite were tested (20, 40, 80, and 160 g per pot). Nitrogen, K, and NO_3-N data were evaluated and response equations were fitted. The results indicated that zeolite enriched with KNO_3 released the macronutrients N and K to lettuce plants. The concentrations of total N, total K, and NO_3-N increased with zeolite levels, and there was a positive correlation between total N and NO_3-N forms. To keep levels of NO_3-N^- in shoots within the safe limit for human consumption, based upon the regression equation for NO_3-N the recommended dose of KNO_3-enriched zeolite should be up to 78 g per plant.

Keywords Growth substrate, *Lactuca sativa*, stilbite

Introduction

New cropping systems, such as tunnels, greenhouses (protected), and hydroponics, are being utilized as alternatives to the traditional field system and have been adopted by vegetable growers. It is also possible to grow plants in synthetic substrates consisting of zeolites with or without peat or vermiculite. The zeoponic system (Mumpton 1999) works as a controlled-release and renewable plant nutrient source (Allen et al. 1995).

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Zeolite minerals are hydrated aluminosilicates of alkali or alkaline-earth metals, structured in a three-dimensional rigid crystalline network, formed by tetrahedral AlO_4 and SiO_4, which come together to compose a system of canals, cavities, and pores. These minerals are characterized by retaining and releasing water and exchanging cations without changes in structure (Mumpton 1999). These minerals can potentially be used in field or in substrate cultivations. There are more than forty species of natural zeolites (Ming and Dixon 1987). The largest zeolite reservoirs in Brazil is found in the Parnaíba River Valley (Rezende and Angelica 1999). The Brazilian sedimetary zeolite is from the stilbite-Ca type (Coombs et al. 1997) with simplified formula of $(Na,K)Ca_2[Al_5Si_{13}O_{36}]\cdot 14H_2O$ (Monte et al. 2009). Bernardi et al. (2013) described this mineral as having the following special properties for agricultural purposes: high cation exchange capacity, high water-holding capacity, and high adsorption capacity.

Zeolites improve the efficiency of nutrient use and affect the nutrient-release dynamics by increasing the availability and reducing losses of nutrients (Allen et al. 1995; Gül, Eroğul, and Ongun 2005; Pickering, Menzies, and Hunter 2002). Mixtures of zeolite and fertilizers have had positive effects on lettuce growth (Gül, Eroğul, and Ongun 2005; Bernardi et al. 2010) and on product quality (Bernardi et al. 2005).

According to Bennini et al. (2002) vegetables represent 72–94 percent of daily nitrate human ingestion. Lettuce plants have a tendency to accumulate nitrate (NO_3) in the leaves (Maynard et al. 1976), and hence there is great interest in monitoring nitrate levels in these plants. The nitrate accumulation in plants depends on several factors such as light intensity, temperature, management, genotypes, availability, and quantity of molybdenum and nitrogen in fertilizer sources (Maynard et al. 1976). There are studies in the literature relating the nitrate content of plants in different cropping systems in Brazil (Bennini et al. 2002; Fernandes et al. 2002; Aquino et al. 2007; Takahashi et al. 2007). However, there is little research dealing with the zeoponic system and the possible effects on the quality of the lettuce. The main objectives of this research were to evaluate effects of the addition of zeolite enriched with potassium nitrate (KNO_3) on the nitrate (NO_3-N) levels of lettuce shoots.

Material and Methods

The experiment was carried out in a greenhouse in 3-kg pots with inert substrate of sand washed with distilled water and hydrochloric acid (HCl) solution (3:1 vv^{-1}). Zeolite was collected in the State of Maranhao, Brazil, in the basin of the Parnaiba River (Rezende and Angelica 1999). The characterization of raw material carried out by Monte et al. (2009) indicated the presence of zeolite stilbite (470 g kg^{-1}) intertwined with smetitic clay with 0.0057 $cm^3\ g^{-1}$ microporous volume, 12.09 $m^2\ g^{-1}$ microporous area, 9.71 $m^2\ g^{-1}$ surface area, 5.09 SiO_2/Al_2O_3 ratio, and 255 meq 100 g^{-1} cation exchange capacity (CEC).

As decribed by Monte et al. (2009), zeolite mineral was ground (<18 mesh) and concentrated by a gravitational process reaching 840 g kg^{-1} of stilbite. A portion of the concentrated material was dispersed into sodium chloride (NaCl) 0.5 mol L^{-1} solution (for saturating the negative charges). Then, this homoionic material was dispersed into KNO_3 (0.5 mol L^{-1}), centrifuged, filtered, and dried. Concentrations of nitrogen (N) and potassium (K) in enriched zeolite were 21,180 and 15,210 mg kg^{-1}, respectively.

Four levels of concentrated and KNO_3-enriched zeolite were tested: 20, 40, 80, and 160 g per pot. There was an extra control treatment without addition of zeolite. The experiment was arranged in a completely randomized block design with three replications. All nutrients were supplied by the nutrient solution (mg L^{-1}): N, 210; phosphorus (P), 31;

Table 1
Amount of nutrients (mg per pot) supplied by treatments

Amount of nutrients	Treatments: KNO_3-enriched zeolite (g per pot) 20	40	80	160	Concentrated zeolite	Control
N	424	847	1,694	3,389	525	525
K	304	608	1,217	2,434	585	585
P, Ca, Mg, S, B, Cu, Fe, Mn, Mo, and Zn[a]	P = 78; Ca = 500; Mg = 120; S = 163; B = 1,25; Cu = 0.05; Fe = 5.0; Mn = 0.5; Zn = 0.5, e Mo = 0.05					

[a]Nutrient solution.

K, 234; calcium (Ca), 200; magnesium (Mg), 48; sulfur (S), 65; boron (B), 0.5; copper (Cu), 0.02; iron (Fe), 5.0; manganese (Mn), 0.5; zinc (Zn), 0.2, and molybdenum (Mo), 0.02 (Sarruge 1975). Potassium nitrate–enriched zeolite treatment did not receive N and K from the nutrient solution. Nutrient solutions were supplied at 100 mL per pot over all cultivation cycles. During the first 30 days of cultivation, a 3-day application interval was adopted and after 50 days, a 1-day interval was used. Plants received water during days in which no nutrient solution was supplied. All the leaching from the pots were recoverded and supplied again to the pots. Nutrient solution composition varied according to treatments, and the nutrients absent in the N-K-enriched zeolites were added by way of a nutrient solution at the same concentration of the control. So, it was ensured that all treatments were supplied with the same quantities of Ca, Mg, S, B, Cu, Fe, Mn, Mo, and Zn. Table 1 summarizes the amount of nutrients supplied by each treatment.

Nursery plants of lettuce (*Lactuca sativa* L. var. Regina) were transplanted to pots 20 days after germination. Lettuce shoots were sampled 60 days after transplanting. Aboveground biomass was cut and dried at 65 °C for 72 h for dry-matter determination. Total concentrations of N and K in shoot samples were determined after hot sulfuric digestion by micro-Kjeldahl and flame-spectrometry procedures (Carmo et al. 2000). The concentrations of NO_3-N in an aqueous extract (200 mg of sample in 20 mL of deionized water) were determined in an ion chromatograph (DIONEX model DX-120; Dionex Corporation, Sunnyvale, Calif.).

Nitrogen, K, and NO_3-N data were tested for differences among treatments using analysis of variance. Equations were adjusted as a function of treatments. Linear correlation coefficients among NO_3-N, N, and K levels were established. Statistical analyses of the data were done using the Statistical Analytical System (SAS) software (SAS Institute, Cary, NC).

Results and Discussion

Figure 1 shows the concentrations (g kg^{-1}) of total N and K in shoots of lettuce grown on substrate with concentrated zeolite, KNO_3-enriched zeolite, and the control (without addition of zeolite). Statistically significant changes were observed in N levels of plants grown with substrate with KNO_3-enriched zeolite. The greatest level calculated (33.6 g kg^{-1}) was obtained at a dose of 160 g per pot of zeolite (Figure 1 A). This value is 22 percent greater

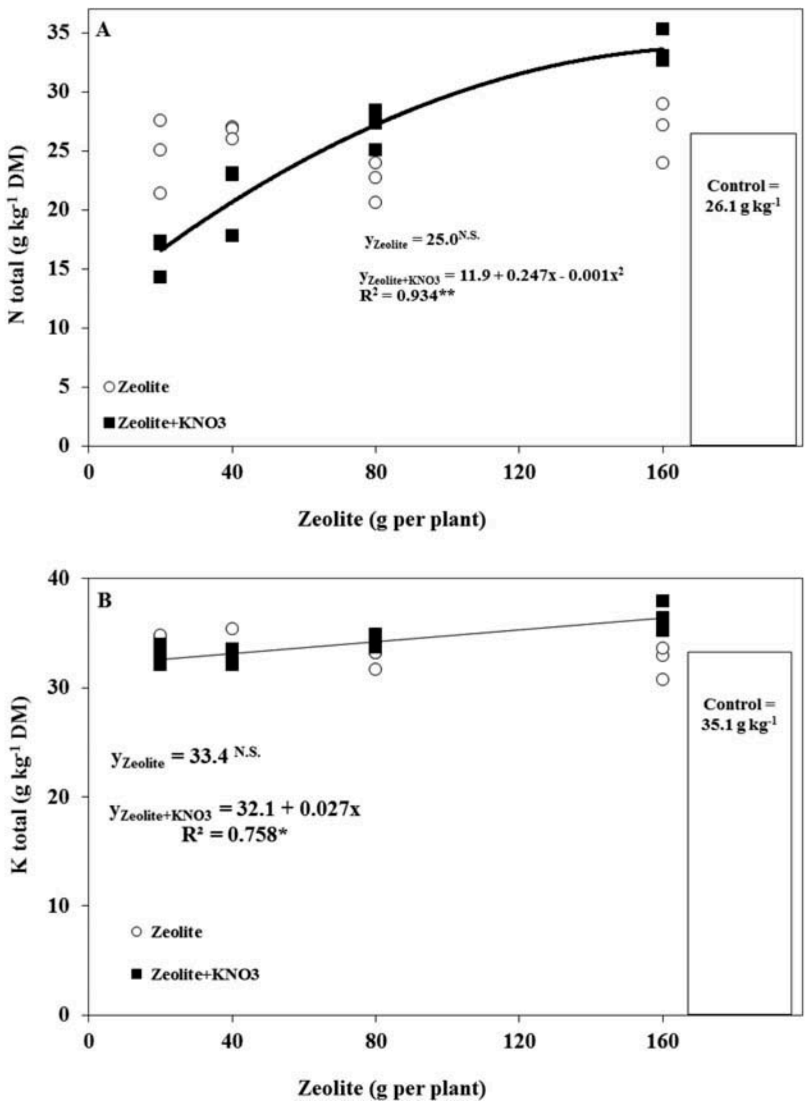

Figure 1. Total concentration (g kg^{-1}) of N (A) and K (B) in lettuce shoots grown in substrate with zeolite.

than the value obtained from the control, which received the nutrients by nutrient solution. Nitrogen contents in shoots observed in this study were lower than those of Fernandes et al. (2002), who found an average value of 47 g kg^{-1} for the same cultivar grown hydroponically. The levels of N and K were also lower than those of Gül, Eroğul, and Ongun (2005), who worked with cultivation substrates with zeolite.

In Brazil, the adequate levels for lettuce range from 30 to 50 g kg^{-1} for N and from 50 to 80 g kg^{-1} for K (Trani and Raij 1996). Thus, the maximum value (33.6 g kg^{-1}) obtained for N was considered adequate, but the maximum value of K (36.7 g kg^{-1}) was considered low. The results indicated that values less than 104 g per pot zeolite may lead to N content below the adequate level. An extra source of K might be necessary to reach appropriate levels of this macronutrient in shoots. This dose is approximately 16 percent greater than the calculated dose for maximum response for dry-matter yield of lettuce described by Bernardi et al. (2010), whose results indicated that 89.2 g per pot of KNO_3-enriched zeolite was the best level.

Significant differences in the concentrations of NO_3-N were observed in treatments with KNO_3-enriched zeolite (Figure 2). Considering the point of inflection of the curve, the greater nitrate content (3,798 mg kg^{-1} DM) was obtained at a dose of 138 g of zeolite-enriched KNO_3 per plant (Figure 1B). These values are approximately twice the value (1700 mg kg^{-1} MS) reported by Fernandes et al. (2002) for the same cultivar. However, the values obtained in the control treatment (1,610 mg kg^{-1}) are equivalent to those observed by Fernandes et al. (2002). The results are also superior to values reported by Bennini et al. (2002) for thirty-two samples of commercial hydroponic lettuce (1,588 mg kg^{-1}), Takahashi et al. (2007) for different nutrient solutions (2,314 mg kg^{-1}), Turazi et al. (2006) for organic and inorganic sources of fertilizer (1,086 mg kg^{-1}), and Aquino et al. (2007) for different degrees of light incidence (2,300 mg kg^{-1}).

According to the limit established by the European community, the levels should be less than 3,000 mg kg^{-1} of NO_3-N in dry matter (McCall and Willumsen 1998). However, the greatest level obtained was approximately 27 percent higher than this limit. Based upon the regression equation for NO_3-N concentration and considering the European Community limitation for NO_3-N, the recommended dose of KNO_3-enriched zeolite should be up to 78 g per plant.

Based on the yield curve published by Bernardi et al. (2010) for lettuce, this dose of KNO_3-enriched zeolite would reach 9.8 g of DM per pot. At the maximal response dose (89.2 g per pot KNO_3-enriched zeolite) the yield was 9.9 g of DM per pot. This 1.0 percent loss in productivity is entirely justified to ensure that the lettuce is safe for human consumption.

The concern with the consumption of products with these compounds comes from the fact the concentration of nitrate is an important index of food quality (Maynard et al. 1976; Luz et al. 2008). Despite some controversy in the recent literature (Luz et al. 2008), nitrates and nitrites can form endogenously ingested N-nitrosamines, potentially

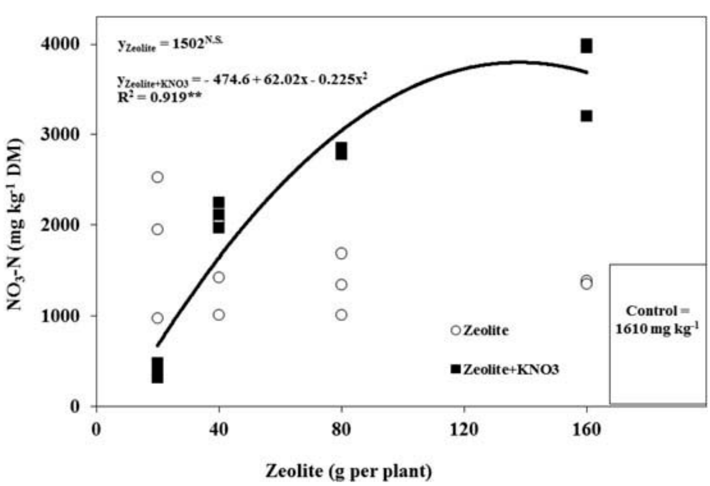

Figure 2. Total levels of NO_3-N^- in lettuce shoot grown in substrate with zeolite.

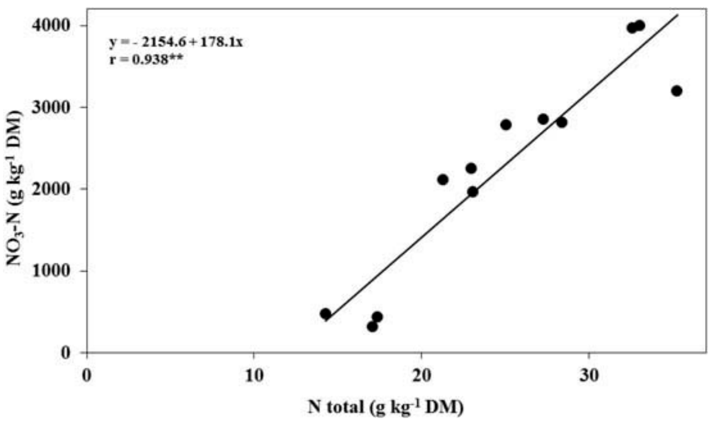

Figure 3. Linear correlation between NO_3-N and N_{total} levels in lettuce shoot grown in substrate with KNO_3-enriched zeolite.

carcinogenic compounds, and methemoglobinemia, preventing the transport of oxygen from the alveoli into the tissues (Maynard et al. 1976). Figure 3 illustrates the direct and highly correlated (r = 93.4 percent) dependence between the concentrations of NO_3-N and total N in lettuce shoots. There was no statistically significant correlation between the K and NO_3-N in shoots of lettuce. According to Maynard et al. (1976) for nitrate to be metabolized in the plant, the first reaction is the reduction to nitrite (NO_2^-), in a reaction catalyzed by nitrate reductase enzyme.

Then the reduction of nitrite to ammonium (NH_4^+) occurs. This form is incorporated initially at the glutamate and glutamine amino acids and then in selected additional organic compounds such as amino acids, pigments, chlorophyll, proteins, hormones, alkaloids, and organic phosphates. Therefore, the accumulation of the NO_3-N ion in plant tissues can occur due to an imbalance between absorption and assimilation.

The results obtained in this study showed that with increasing supply of NO_3-N, the capacity of reducing the nitrate in the roots probably become a limiting factor and led to an increase in the proportion of total N transported to the air in the form of NO_3-N. As the fate of N is preferentially to the leaves, the more photosynthetically active organs, lettuce plants are at risk of nitrate accumulation in leaves that exceed concentrations for human consumption.

These results indicate the possibility to reduce the NO_3-N concentration in lettuce leaves by reducing the doses of nitrate supplied during the vegetative growth cycle of the culture, confirming the previous results of McCall and Willumsen (1998), Fernandes et al. (2002), and Takahashi et al. (2007). Furthermore, these authors assert that the reduction of NO_3-N in lettuce leaves can also be achieved with increasing light intensity, harvesting during or shortly after a period of high luminosity, delay in harvest time, use of cultivars with less ability to accumulate nitrate, and provision of NH_4^+ and/or Cl^- in the fertilizer.

These results indicate the technical feasibility of providing N and K via KNO_3-enriched zeolite. The optimal dose (78 g per pot) afforded suitable yield and product quality. These results confirm that the Brazilian zeolite has adequate characteristics, which are comparable to other zeolites sources (Allen et al. 1995; Gül, Eroğul, and Ongun 2005).

Conclusions

The results indicated that zeolite enriched with KNO_3 released the macronutrients N and K to lettuce plants. The concentrations of total N, total K, and NO_3-N increased with zeolite levels, and there was a positive correlation among these forms of N. To keep levels of NO_3-N^- in shoots within the safe limit for human consumption, the dose was found to be 78 g per plant.

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