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Zeolite influences on nitrate leaching, nitrogen-use efficiency, yield and yield components of canola in sandy soil

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With regard to the low cation-exchange capacity and large saturated hydraulic conductivity of sandy soils, a field experiment was carried out in 2006–2007 to determine the impact of zeolite on nitrogen leaching and canola production. Four nitrogen (N) rates (0, 90, 180, and 270 kg ha⁻¹) and three zeolite amounts (3, 6 and 9 t ha⁻¹) were included as treatments. The results demonstrated that the highest growth parameters and seed yield were attained with 270 kg N ha⁻¹ and 9 t zeolite ha⁻¹. However, the highest and the lowest seed protein percentage and oil content were obtained with 270 kg N ha⁻¹ accompanied by 9 t zeolite ha⁻¹, respectively. Nitrate concentration in drained water was affected by nitrogen and zeolite. The lowest and highest leached nitrate values were found in control without N and zeolite (N₀Z₀) and in treatments with the highest N supply without zeolite (N₂₇₀Z₀), respectively. In general, nitrogen-use efficiency decreased with an increase in N supply. Application of 9 t zeolite ha⁻¹ showed higher nitrogen use efficiency than other zeolite amounts. Also, application of more N fertilizer in soil reduced nitrogen uptake efficiency. In total, application of 270 kg N ha⁻¹ and 9 t zeolite ha⁻¹ could be suggested as superior treatment.

Keywords: canola; nitrogen leaching; sandy soil; yield; zeolite

Introduction

Nitrogen is an essential key nutrient needed to increase and maintain worldwide agriculture production (Li et al. 2007). The use of nitrogen fertilizer in agricultural countries has grown rapidly. Unfortunately, the widespread use of nitrogen fertilizer is not entirely free from risk. Under some conditions, especially in sandy soils, intensive use of nitrogen fertilizers may lead to nitrate leaching, which in turn means that drinking water may become a health hazard and in addition increased nitrogen supply to crops may reduce economic returns.

Winter canola (*Brassica napus* L.) is widely grown as an oilseed in the world (Ozer 2003). In general, it needs high amount of nitrogen but is characterized by low nitrogen efficiency, which is defined as seed dry weight produced per unit of accumulated nitrogen fertilizer (Rathke et al. 2006). Compared with cereals, winter canola requires a higher amount of nutrients, and available nitrogen frequently limits seed yield

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(Rathke et al. 2005). Clonenne et al. (2002) proposed that canola has a higher critical nitrogen demand for biomass formation than wheat. To produce 0.1 t of seeds, the whole crop accumulates ~6 kg of nitrogen (Rathke et al. 2006). Therefore, cropping of winter canola is characterized by high nitrogen surpluses resulting from nitrogen fertilization exceeding seed nitrogen demand (Dreccer et al. 2000; Rathke et al. 2006). Excessive nitrogen fertilization and other management practices can potentially lead to high nitrate leaching losses (Di and Cameron 2002). As a result, evidence of increasing nitrate-leaching losses from soil under various land-use systems has increased the interest and need to find better mitigating strategies (Silva et al. 2004). Maximum plant growth and realization of yield potential depends on the soil characteristics covering the biological, chemical and physical conditions necessary for the root system to maximize plant-required absorption of nutrients and water, and enable biochemical reactions that occur in the root (Barber 1984).

The sandy soils on which canola is commonly grown, especially in Iran, provide favorable physical properties, such as minimum compaction tendency and good aeration, but nutrient retention is generally poor and water-soluble nutrients like nitrogen are prone to leaching. To obtain high optimal yield in such soils, high rates of nitrogen are often applied. Soil characteristics and management factors, together with unpredictable rainfall events or excess irrigation during the growing season, often in result large NO_3^- leaching losses (Zvomuya et al. 2003).

Historically, organic materials such as manure have been mixed with sandy soil to improve water and nutrient retention (Bigelow et al. 2004). One disadvantage of organic amendments is that they decompose over time, reducing their beneficial effects (Bigelow et al. 2004). The ideal amendment should be relatively stable to provide water and nutrient retention and release that are comparable with organic amendments. In recent years, more common products like porous ceramics, diatomaceous earth and zeolites have been increasingly used as inorganic soil amendments. Some of the characteristics of these products that potentially make them desirable for improving the properties of soft soils are a large internal porosity that results in water retention, uniform particle size distribution that allows them to be easily incorporated and high cation-exchange capacity (CEC) that retains nutrients (Ok et al. 2003; Bigelow et al. 2004). The unique physical and chemical properties of natural zeolites, in combination with their abundance in sedimentary deposits and rocks derived from volcanic parent materials, have made them useful in many industrial applications. These properties have also increased their use in agronomic and horticultural applications (Dwairi 1998). Zeolites are natural minerals, first discovered in 1756 by a Swedish mineralogist, who named the porous minerals from the Greek words meaning 'boiling stone' (Mumpton 1999). They are hydrated aluminosilicates, characterized by three-dimensional networks of SiO_4 and AlO_4 tetraeder, linked by sharing of all oxygen atoms. Partial substitution of Si^{4+} by Al^{3+} leads to an excess of negative charge, which is compensated by cations. Within the structure of natural zeolite, water and cations can be reversibly removed or replaced by other cations (Rehakova et al. 2004). Clinoptilolites are one type of zeolite, and although not the most well known, are one of the most useful. Extensive deposits of clinoptilolites are found in western USA, Bulgaria, Hungary, Japan, Australia and Iran (Mumpton 1999). The size of clinoptilolite channels controls the size of molecules or ions that can pass through them and, therefore, a zeolite like clinoptilolite can act as a chemical sieve allowing some ions to pass through while blocking others (Mumpton 1999). Amendment of clinoptilolite zeolite to sandy soils has been reported to lower the nitrogen

concentration in the leachate and to increase moisture and nutrients in the soil due to increased soil surface area and CEC (He et al. 2002). In addition, clinoptilolite zeolite is a more permanent addition to the root zone, demonstrating good stability in weathering, impact and absorption tests (Ok et al. 2003). There is no comprehensive information on the use of natural clinoptilolite zeolite under farmers' conditions for reducing NO_3^- leaching and improving canola yield in sandy soils.

The objectives of this study were to evaluate the effect of clinoptilolite zeolite and nitrogen fertilizer on winter canola production and their effect on NO_3^- leaching from rooting zone. Our hypothesis was that the zeolite application decreases NO_3^- leaching and would improve growth and canola seed yield in sandy soils.

Materials and methods

Experimental site

The experiment was conducted at the research farm of Tarbiat Modares University, Tehran, Iran ($35^\circ 41' \text{ N}$, $51^\circ 19' \text{ E}$ and 1215 m above sea level) in the 2006–2007 growing season. Daily meteorological data, including air temperature and precipitation, were obtained from the nearest weather station (500 m away) (Figures 1 and 2). The long-term mean annual precipitation (30-year) in the region is 298 mm, which mainly occurs in autumn and winter. The long-term mean annual temperature is 18.8°C .

Soil and water analysis

Before planting, several soil samples were taken at depths of 0–30 and 30–60 cm, and a composite sample was collected from each soil layer, air dried, crushed and analyzed for physical and chemical properties (Table 1). The research field had a sandy loam soil based on the textural triangle classification (Gee and Bauder 1986). Irrigation water, originating from a local well, was of good quality (electrical conductivity and pH were 0.6 dS m^{-1} and 7.8, respectively).

Land preparation and treatments establishment

The preceding crop was sweetcorn (*Zea mays* L.). The field was prepared using a shallow plow followed by disking in autumn. Each experimental unit consisted of ten

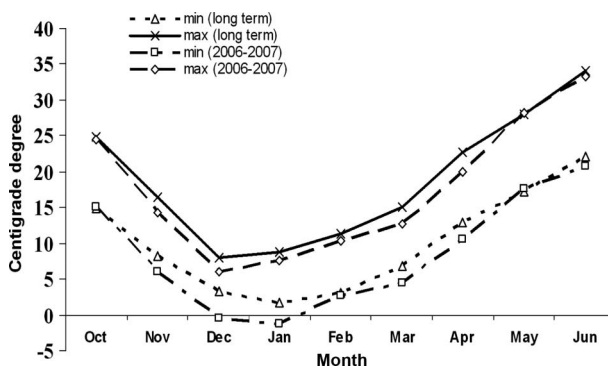


Figure 1. Temperature changes during growing season (2006–2007).

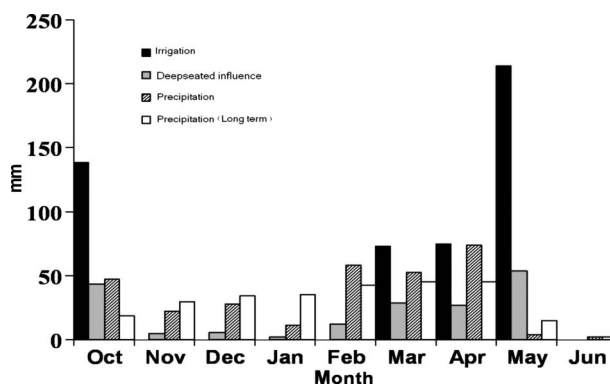


Figure 2. Precipitation, irrigation and deep-seated influence changes during growing season (2006–2007).

Table 1. Soil chemical properties at two soil depths.

Properties	Depth (cm)	
	0–30	30–60
Organic matter (%)	0.8	0.7
pH (water 1:2 ratio)	7.7	7.2
Sand (%)	65	58
Silt (%)	23	25
Clay (%)	12	17
EC (dS m ⁻¹)	1.5	1.7
N (%)	0.09	0.11
P (mg kg ⁻¹)	> 12	n.d.*
K (mg kg ⁻¹)	> 350	n.d.
Fe (mg kg ⁻¹)	7.6	n.d.
Zn (mg kg ⁻¹)	1	n.d.
Cu (mg kg ⁻¹)	0.7	n.d.
CEC (meq (100 g) ⁻¹)	6.4	n.d.

Note: *Not determined. CEC, cation-exchange capacity.

4-m-long rows, 0.3 m apart. Two- and one-meter spaces between the blocks and plots were considered to avoid lateral movement of water from one plot to the next. Polyethylene pipeline and a counter were installed to control irrigation amount. The experimental design was laid out as a randomized complete block with a factorial arrangement of treatments in three replications. Three nitrogen levels (90, 180 and 270 kg N ha⁻¹ applied as urea) were factor A and four levels of zeolite (0, 3, 6 and 9 t-ha⁻¹) were factor B. These rates of nitrogen reflect feasible inputs (low, mean and high) currently used in canola production (Rathke et al. 2006) and the rates of zeolite have been proposed by Mumpton (1999). In addition, in each block, one plot was considered as the control (no nitrogen and zeolite). Abbreviations for the treatments are given in Table 2.

A zeolitized volcanic tuff containing K–Ca clinoptilolite with an CEC of ~200 meq (100 g)⁻¹ was used. In this study, zeolite was provided from a quarry in the Mianeh city in the north east of Iran and was composed of ~90% clinoptilolite, with the rest made up of volcanic glass, clay minerals, quartz and feldspar. X-Ray

Table 2. Abbreviations for treatments.

Abbreviation	Treatment
N ₉₀ Z ₀	90 kg N ha ⁻¹ + 0 t ha ⁻¹ zeolite
N ₁₈₀ Z ₀	180 kg N ha ⁻¹ + 0 t ha ⁻¹ zeolite
N ₂₇₀ Z ₀	270 kg N ha ⁻¹ + 0 t ha ⁻¹ zeolite
N ₉₀ Z ₃	90 kg N ha ⁻¹ + 3 t ha ⁻¹ zeolite
N ₁₈₀ Z ₃	180 kg N ha ⁻¹ + 3 t ha ⁻¹ zeolite
N ₂₇₀ Z ₃	270 kg N ha ⁻¹ + 3 t ha ⁻¹ zeolite
N ₉₀ Z ₆	90 kg N ha ⁻¹ + 6 t ha ⁻¹ zeolite
N ₁₈₀ Z ₆	180 kg N ha ⁻¹ + 6 t ha ⁻¹ zeolite
N ₂₇₀ Z ₆	270 kg N ha ⁻¹ + 6 t ha ⁻¹ zeolite
N ₉₀ Z ₉	90 kg N ha ⁻¹ + 9 t ha ⁻¹ zeolite
N ₁₈₀ Z ₉	180 kg N ha ⁻¹ + 9 t ha ⁻¹ zeolite
N ₂₇₀ Z ₉	270 kg N ha ⁻¹ + 9 t ha ⁻¹ zeolite
N ₀ Z ₀	Control

Note: N, nitrogen; Z, zeolite.

spectrophotometer analysis showed that the clinoptilolite of Mianeh is of the K–Ca type with low Na⁺ content. Other chemical indices of this zeolite are presented in Table 3.

Nitrogen fertilizer was split into three equal amounts and applied before sowing, at the beginning of stem elongation and at the flowering stage. All zeolites were broadcasted on the soil surface of each plot and incorporated. Trifluralin at 3.5 L ha⁻¹ was sprayed and incorporated into the soil by disking. Potassium and phosphorous fertilizers were not applied as there were enough amounts of these nutrients in the soil (Table 1).

Canola seeds (*Brassica napus* L. C.V. Okapi) were sown on 4 October at a density of ~830,000 plants ha⁻¹. A systemic pesticide (Metasystox) was used at the flowering stage of canola to protect against aphids. Irrigation was performed immediately after sowing. This operation was done in a manner that would avoid run-off. Irrigation scheduling was performed according to daily changes in soil water content (ΔS_w) at the rooting depth of the crop. This procedure uses as a deficit approach (soil water content at field capacity, FC, represents no deficit), to estimate irrigation requirements. Whenever the daily soil water deficit value reached 50% of the total available soil water, the plots were irrigated. The 60-cm soil depth was chosen according to Kjellström (1991) who stated that the highest root dry matter and of winter canola occurred in 0–60-cm soil depth.

It's noticeable that the volumetric soil water content of each plot was monitored daily from soil surface to a depth of 60 cm (at 0.2-cm intervals) using Time-Domain Reflectometry (TDR; FM-Trime-IMKO-GmbH, Germany). TDR tube access probes were inserted into holes created in the middle of each experimental unit. Volumetric soil water content data were collected daily during the growing season, whereas in winter the measurements were done weekly.

Simultaneous with TDR tube access probe installation (before sowing), vertical holes of 5 cm diameter and 65 cm depth were created by a hand auger in the middle of each plot and soil water sampler tubes (Model 1900, Soil Moisture Equipment Co.) were inserted into the holes. To avoid possible contamination, ceramic caps of the soil water sampler tubes were washed before inserting. To create good contact between ceramic cap and soil, the gaps were filled with soft soil.

Table 3. Chemical analysis of the applied zeolite (%).

Constituent	Amount (%)
SiO ₂	65
Al ₂ O ₃	12.02
K ₂ O	3
Na ₂ O	1.08
MgO	0.1
CaO	2.3
Fe ₂ O ₃	1.5
MnO	0.04
P ₂ O ₅	0.01
Cation-exchange capacity	200 meq (100 g) ⁻¹

Soil water sampling and analysis

Determining solute leaching loss requires two sets of information: (1) quantity of the drainage flux and (2) solute concentration in the drainage solution.

A portable vacuum pump (Model 2005 G2, Soil Moisture Equipment Co.) was used to apply -30 KPa tension for collecting water sampler every 4–6 days or when drainage was suspected to occur such as after rainfall or irrigation (when soil–water content exceeded FC). Water samples were taken from soil water sampler tubes by a thin vessel of collection using a vacuum hand pump. The samples were acidified by sulfuric acid (1 ml l⁻¹) and stored in a refrigerator until NH₄⁺ and NO₃⁻ analysis. Water samples were analyzed for NH₄⁺ and NO₃⁻ concentrations using cadmium and salicylate methods respectively, by means of a spectrophotometer (Model dr/2500, Hach Co.). For measurement of daily deep percolation, water balance equation identified by Errebhi et al. (1998) was used (Equation 1).

$$\text{Daily deep percolation} = P + I - \Delta S_W - ET_C - R \quad (1)$$

where P is precipitation (mm), I is the irrigation water applied (mm), ΔS_W is the daily changes of soil water content (mm) in rooting depth (measured by TDR), ET_C is evapotranspiration (mm) and R is run-off (since irrigation cycle in each plot was closed there was no run-off during experiment). Percolation occurs whenever $(P + I)$ is higher than $(\Delta S_W + ET_C)$ (Errebhi et al. 1998). Input from irrigation and rainfall were measured at the experimental site. Crop evapotranspiration was calculated daily according to Equation (2):

$$ET_C = ET_0 \times K_C \quad (2)$$

where ET_0 is the reference evapotranspiration calculated using the FAO–Penman–Monteith method (Allen et al. 1998) and depended on daily weather conditions at the experimental site, whereas K_C , the crop coefficient, depends on the growth stage of the crop. The initial soil–water storage was equal to soil water holding capacity to 60 cm deep (before sowing, when soil profile was fully charged), and subsequent ΔS_W was determined on a daily basis.

The mineral nitrogen leached below the rooting zone (N_{leach}) was obtained by multiplying percolation (drainage, D) with measured value of nitrogen concentration (NC) with the suction cups located at 70 cm depth (Equation 3) (Li et al. 2007)

$$N_{\text{leach}} = \sum D \times \text{NC} \quad (3)$$

Plant measurements

In order to find out the time-trend of leaf expansion, leaf area was measured at seven growth stages in days after sowing (DAS): 30, 60, 80, 90, 195, 210, 270 DAS by means of a leaf area meter (Delta-T area meter; Delta-T Devices Ltd, Cambridge, UK).

Chlorophyll content were performed at four growth stages (60, 90, 150, and 180 DAS) with a handheld dual-wavelength meter (SPAD-502 Minolta, Japan) on 30 younger fully expanded leaf blades chosen in each plot.

Four square meters of each plot was hand-harvested on 6 June when 30–40% of seeds had turned from green to brown or black (Ozer, 2003). Then plant height, number of secondary branches and total dry matter were determined. In order to evaluate dry matter, harvested plants were separated into seed and straw. They were oven-dried at 60°C for 72 h to constant weight. Yield and yield components including pod number per m², seed number per sliques and 1000-seed weight at 10% moisture (Ozer, 2003) were measured at physiological maturity. Harvest index was determined by dividing seed dry matter with above ground biomass. The oil and protein contents of the seeds were determined using a NIR analyzer (Inframatic 8620 Percor, Germany).

Plant samples were ground in mill and passed through a 2-mm sieve. Subsamples (200 g) of plant material were digested using a Kjeldhal method before analysis for total nitrogen. The digestion mixture included 0.5% selenium as a catalyst and salicylic acid. Nitrogen uptake by grain and straw were calculated by multiplying their respective yield with their nitrogen content.

The following N-efficiency parameters were calculated for each treatment (Hermanson et al. 2000; Fan et al. 2004; Lopez-Bellido et al. 2005).

- Nitrogen-efficiency ratio (NER; kg kg⁻¹): as the ratio of grain yield to N uptake by grain;
- Nitrogen-use efficiency (NUE; kg kg⁻¹): as the ratio of grain yield to N supply;
- Nitrogen-uptake efficiency (NUpE; kg kg⁻¹): as the ratio of total plant N uptake to nitrogen supply.

Statistical analysis of data

All data were analyzed using the ANOVA procedure in SAS software (SAS Institute 2002). Assumptions of variance analysis were tested by ensuring that the residuals were random, homogenous, with a normal distribution about a mean of zero. When F -test indicated statistical significance at the $p < 0.01$ or $p < 0.05$ level, the protected Least Significant Difference (protected LSD) was used to separate the means.

Results and discussion

Weather condition

Precipitation, total volume of water used for crop irrigation and drainage during canola growth (in monthly pattern) compared with precipitation data averaged across the past 30 years are illustrated in Figure 1. Figure 2 indicates the monthly minimum and maximum air temperature during the canola growing season compared with data averaged across 30 years. Total precipitation during the experiment was 297 mm, an 11% increase over the long-term average. The distribution of rainfall during the growing season was similar to the long-term pattern, in that >50% of the total rainfall occurred between February and April. Moreover, the lowest and highest rainfall during this experiment fell in June and April, respectively. Twenty percent of the total drainage was obtained in October, 14% from November to February, and 61% from March to May. Minimum drainage was measured from November to February because no irrigation was applied. The lowest and highest air temperature during the experiment was recorded in January (-1.25°C) and June (33.29°C), respectively. These results are similar to long-term averaged values from the meteorological records.

Leaf area index (LAI)

Different nitrogen levels caused significant differences on leaf expansion (Figure 3). In the early growing season, leaf area index (LAI) was strongly increased and maximum LAI was observed at 60% flowering, thereafter LAI decreased due to senescence and leaf abscission. At 30 DAS nitrogen had no significant effect on LAI, but at 180 and 195 DAS the difference between N_{270} and N_{90} was greatest. According to Radin and Parker (1979), the effect of nitrogen on leaf size is mostly mediated by cell size. Radin and Boyer (1982) suggested that one of the main reasons for slower leaf expansion under nitrogen-limiting conditions is decreased hydraulic conductance, which limits water delivery to growing leaves. Leaf sampling at 195 and 270 DAS showed larger decrease of LAI in 90 kg N ha^{-1} treatment compared with 270 kg N ha^{-1} . Similarly, zeolite had no significant effect on LAI at 30 and 60 DAS (Figure 4). Measurements at 30 and 60 DAS showed that the highest LAI was obtained from no zeolite treatment as this treatment increased LAI by 21%

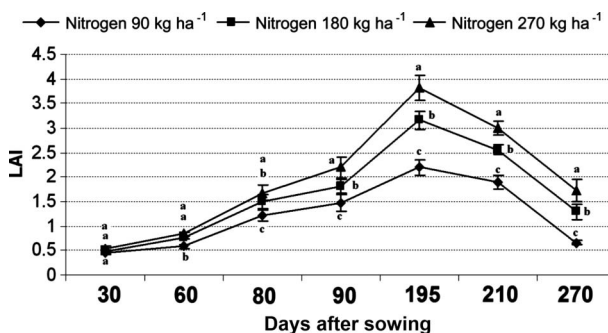


Figure 3. Leaf area index (LAI) of canola dependence on different nitrogen levels and days after sowing. All values followed by the same letter are not statistically different at $p < 0.05$.

compared with 9 t zeolite ha⁻¹ treatment (Figure 4). Because nitrogen is more available during the early growing season, plants were not envisaged to lack of nitrogen, while nitrogen was absorbed by zeolite and was temporarily inaccessible to plants, especially in the 9 t zeolite ha⁻¹ treatment. The LAI slope at 180 DAS was less in zeolite-treated plants than in non-treated plants (Figure 4). It seems that nitrogen was released slowly by zeolite at times of deficiency, which usually occurs after flowering. The increase in LAI could be related to increase in leaf area duration. Notability of leaf perpetuity in canola, especially at the end of growing season, is emphasized by Hocking et al. (2002).

Chlorophyll content

The effects of nitrogen and zeolite amounts on chlorophyll content are shown in Figures 5 and 6. Chlorophyll variations were approximately stable except for 150 DAS. Peng et al. (1996) reported that chlorophyll content (SPAD) was relatively stable during plant growth. The increase in chlorophyll at 150 DAS compared with 90 and 180 DAS could be attributed to the plant growth stage. SPAD values at 150 DAS coincided with rosette stage, and were therefore increased due to the dense

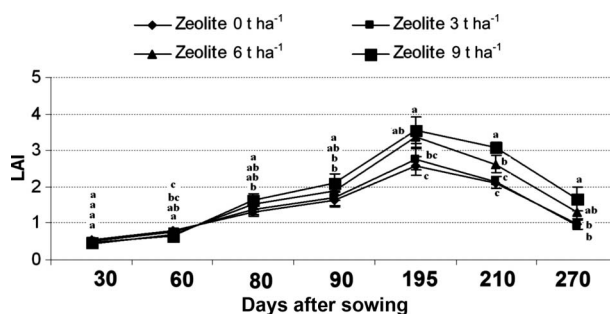


Figure 4. Leaf area index (LAI) of canola dependence on different zeolite levels and days after sowing. All values followed by the same letter are not statistically different at $p < 0.05$.

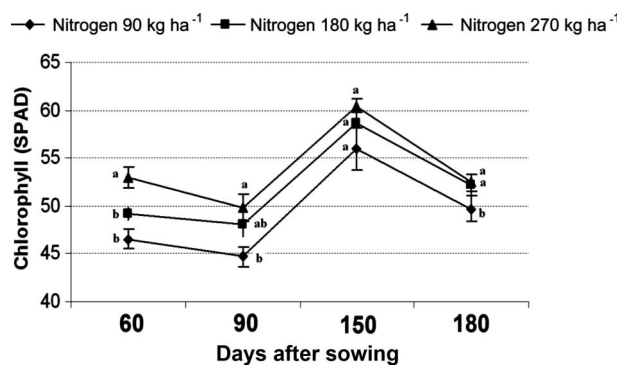


Figure 5. Chlorophyll content (SPAD value) of canola dependence on nitrogen rates and days after sowing. All values followed by the same letter are not statistically different at $p < 0.05$.



Figure 6. Chlorophyll content (SPAD value) of canola dependence on zeolite rates and days after sowing. All values followed by the same letter are not statistically different at $p < 0.05$.

protoplasm as a consequence of cold tolerance. Furthermore, specific leaf area (SLA) calculations (data not shown) showed that SLA decreased more at 150 DAS than at 90 and 180 DAS. The increase in leaf thickness caused a decrease in SLA and light transmittance, as shown by chlorophyll meter, such that the chlorophyll content in the ground area was increased. Because SPAD values are an indirect measure of the chlorophyll content of a leaf and are based on the amount of absorption of red light (~ 650 nm), a thick leaf, which usually has a large specific leaf weight (SLW) and likely greater chlorophyll content on a per area basis, should absorb more light than a thin leaf (Peng et al. 1995). Application of 270 kg N ha^{-1} significantly increased SPAD compared with leaves in the 90 and 180 kg N ha^{-1} treatment (Figure 5). Results obtained by Yang et al. (2003) agree with our findings. At early measurements (60, 90 and 150 DAS), zeolite applications increased chlorophyll, although the increase was not significant (Figure 6). At 180 DAS, chlorophyll measurement was carried out after top dressing. Under such situations, nitrogen was probably absorbed by zeolite, so the highest chlorophyll content was found by plants that were not treated by zeolite (Figure 6).

Plant height

The tallest (147.91 cm) and shortest (114.76 cm) plants were attained from treatments N_{270}Z_9 and N_0Z_0 , respectively (Table 4). There was a linear relationship between different nitrogen amounts and plant height. Application of $9 \text{ t zeolite ha}^{-1}$ increased plant height significantly compared with other application levels. An increase in canola height by nitrogen has been reported by Ozer (2003). The positive effect of zeolite on plant height can be attributed to the improvement in nitrogen absorption.

Number of branches

In plants treated with N_{270}Z_9 , the numbers of branches were drastically increased compared with other treatments. The increase in this trait was parallel with the increments in nitrogen and zeolite rates (Table 4). Sing and Bhargava (1994) reported that nitrogen had a significant effect on the increase in the number of branches in canola. It has been identified that nitrogen use stimulates lateral buds growth and vegetative stage duration. The increment in branch number of canola in response to nitrogen fertilizer is due to better plant growth and development. In

contrast, nitrogen deficiency causes poor growth and a smaller canopy due to less branching (Rathke et al. 2006). It seems that joined application of zeolite with nitrogen fertilizer increases soil CEC, and as a result, it increases nutrient retention capacity and consequently plant growth.

Total dry matter (TDM)

Results showed that TDM was significantly influenced by treatments. The highest ($8828.7 \text{ kg ha}^{-1}$) and lowest ($5274.9 \text{ kg ha}^{-1}$) amounts of canola TDM were obtained from N_{270}Z_9 and N_0Z_0 (control) treatments, respectively (Table 4). TDM was increased significantly with increase of nitrogen and zeolite application. Changes in biomass production in response to nitrogen supply have been observed in canola (Svecnjak and Rengel 2006). Variation in biomass production in canola as a result of nitrogen availability could be attributed to the increase in the amount of cumulative intercepted radiation by the canopy, radiation use efficiency and better dry matter partitioning among different organs (Dreccer et al. 2000). Actually, nitrogen availability increases radiation interception due to an increase in crop growth rate and LAI, and thus photosynthesis, carbon fixation and finally dry matter production. Moreover, zeolite acts as a preventer of nitrogen leaching and increases CEC (He et al. 2002), thus improving the availability of nitrogen over a long time.

The change in dry matter in response to different nitrogen levels was linear, whereas it was both linear and quadratic in response to different zeolite amounts (Table 4). The linear relationship between dry matter and nitrogen reflects the tendency of canola to exhibit an indeterminate growth habit when nutrients are essentially unlimited with no heat stress (Jackson 2000).

Seed yield

The lowest ($1038.3 \text{ kg ha}^{-1}$) and highest ($2452.3 \text{ kg ha}^{-1}$) canola seed yield were achieved from N_0Z_0 and N_{270}Z_9 treatments, respectively. In addition, N_{270}Z_9 treatment showed a noticeably higher seed yield compared with N_{270}Z_0 (30% increase), N_{270}Z_3 (27% increase) and N_{270}Z_6 (20% increase) treatments. Increase in the nitrogen application rate significantly increased seed yield while application of zeolite up to 6 t ha^{-1} increased seed yield non-significantly (Table 4). The positive impact of nitrogen on the seed yield of winter canola has also been described elsewhere (Ozer 2003; Rathke et al. 2005).

Pod numbers per square meter

An increase in nitrogen application rate causes increases in LAI and leaf area duration (LAD) (Wright et al. 1988) and, therefore, seed yield increases. In this study the highest correlation ($r^2 = 0.75^{**}$) was obtained between seed yield and pod number per square meter. An increase in pod number increases the final seed yield because more pods could be develop a stronger sink size. Furthermore, pods play an important role in photosynthesis and the remobilization of assimilates in the late crop growing period when the leaves are almost in senescence. In addition, the chemical and physical properties of zeolite enhanced the capacity of soil to absorb and then slowly release nutrients, especially nitrogen, to the plants (He et al. 2002). The number of pods per square meter increased significantly in response to the

Table 4. Effect of nitrogen and zeolite application rates on plant height, number of branches, total dry matter, seed yield, pod number per m², number of seed per pod and 1000 seed weight.

Nitrogen (kg ha ⁻¹)	Zeolite (t ha ⁻¹)	Plant height (cm)	Number of branches	Total dry matter (g)	Seed yield (kg ha ⁻¹)	Pod number in m ⁻²	Number of seed in pod	1000 seed weight (g)
0	0	114.76	4.63	5274.91	1038.30	33.08.81	14.30	2.96
90	0	124.19	6.48f	6575.62	1569.31	5654.01	27.70	3.14
180	0	131.78b	7.91	7162.80	1811.53	6190.72	22.91	3.36
270	0	139.15	9.41	7550.51	1896.25	8630.41	17.83	3.53
90	3	126.33	7.45	6523.00	1531.90	6654.02	26.77	3.10
180	3	132.53	7.66	7181.70	1856.76	7493.32	22.17	3.35
270	3	138.03	10.53	7700.55	1951.52	8753.82	17.78	3.57
90	6	129.71	7.50	6473.31	1502.81	6528.25	25.26	3.19
180	6	136.66	10.16	7384.87	1903.12	8691.92	20.81	3.43
270	6	139.28	11.25	8239.32	2055.32	9616.92	17.00	3.64
90	9	132.76	8.01	6985.86e	1637.63	6838.42	23.13	3.22
180	9	141.78	10.16	8003.92	2228.22	8920.51	18.86	3.24
270	9	147.91	14.10	8828.74	2452.34	10800.31	15.86	3.70
Mean		133.45	8.86	7219.81	1802.66	7621.63	20.80	3.34
p-value		0.002	0.001	0.001	0.001	0.001	0.002	0.8892
LSD		12.91	2.61	656.01	208.89	1226.90	5.29	0.93
SE		2.93	0.43	182.68	64.54	315.74	0.78	0.08
Nitrogen application rate (kg ha ⁻¹)								
90		128.25	7.36	6632.70	1560.40	6418.72	25.71	3.16
180		135.69	8.97	7433.30	1949.89	8074.11	21.19	3.49
270		141.09	11.32	8079.70	2088.80	9450.42	17.12	3.62
P-value		0.001	0.001	0.001	0.001	0.001	0.001	0.1782
LSD		4.19	1.34	317.5	105.16	587.76	2.70	0.48
Linear		**	**	**	**	**	**	ns
Quadratic		ns	ns	ns	**	ns	ns	ns

(continued)

Table 4. (Continued).

Nitrogen (kg ha ⁻¹)	Zeolite (t ha ⁻¹)	Plant height (cm)	Number of branches	Total dry matter (g)	Seed yield (kg ha ⁻¹)	Pod number in m ⁻²	Number of seed in pod	1000 seed weight (g)
Zeolite application rate (t ha ⁻¹)								
0		131.71	7.93	7096.30	1759.00	7158.43	22.81	3.34
3		132.29	8.55	7135.00	1780.05	7633.73	22.24	3.34
6		135.22	9.63	7365.80	1820.39	8279.04	21.02	3.42
9		140.82	10.76	7930.50	2106.01	8853.16	19.28	3.39
<i>p</i> -value		0.002	0.005	0.003	0.001	0.002	0.1221	0.9879
LSD		4.84	1.55	366.61	121.43	678.68	3.12	0.56
Linear		**	**	**	**	**	*	ns
Quadratic		ns	ns	*	**	ns	ns	ns
Significance								
N ₀ Z ₀ vs. N _x Z _x		**	**	**	**	**	**	ns
N _x Z ₀ vs. N _x Z _x		ns	ns	ns	ns	ns	ns	ns
N _x Z ₀ vs. N _x Z ₉		ns	ns	**	**	**	*	ns
N × Z interaction								
<i>p</i> -value		0.9500	0.4627	0.4303	0.0702	0.3658	0.9955	0.9994

Note: Significant at the *0.05 and **0.01 probability levels. ns, not significant.

increased nitrogen amount (Table 4). The highest pod number per square meter (10,800.3) was achieved with treatment $N_{270}Z_9$. The number of pods per plant is one of the major determinants of canola yield and it depends on the number of flowers produced by plant (Ozer 2003). Rathke et al. (2006) showed that an external nitrogen supply by means of nitrogen fertilizers increases both LAI and crop growth rate (CGR), resulting in a higher number of pods per plant. Cheema et al. (2001) reported that the number of pods per plant was increased by increasing nitrogen application rates. In our experiment, application of 9 t zeolite ha^{-1} increased siliqua number by 24% compared with control (Table 4). It is reasonable to assume that increment of nitrogen absorption by plants may be a consequence of reduction in nitrogen leaching due to zeolite application.

Seed number per pod

The lowest and highest numbers of seeds per pod were obtained from treatments N_0Z_0 and $N_{90}Z_0$, respectively (Table 4). In general, seed number was reduced by the increase in nitrogen and zeolite application rates. However, difference among treatments was not significant (Table 4). It seems that sink–source relations play an important role in reducing seed number. Results showed that the number of lateral branches and pods increased with the increase in nitrogen and zeolite application rates, but the number of seeds per pod decreased. This can be attributed to the inability of the source to assimilate the supply. A negative and significant correlation between number of seeds per pod and number of lateral branches ($r^2 = -0.61^{**}$), and between number of seeds per pod and the number of pods ($r^2 = -0.69^{**}$) is subsidiary of this finding (Table 4). Hocking et al. (2002) have also mentioned the effect of high nitrogen levels on source limitation of canola at the end of growing season. Actually, relationships between yield components are determinant of yield so that increase in one component is companion with decrease in other components.

Thousand seed weight

The effect of treatments was not significant for 1000-seed weight (Table 4). The 1000-seed weight varied from 2.96 in N_0Z_0 to 3.7 g in $N_{270}Z_9$. The increase in seed yield was not significant as a result of nitrogen and zeolite applications. Svecnjak and Rengel (2006) reported that 1000-seed weight rarely responds to nitrogen fertilization because grain filling usually coincides with the period of highest nitrogen mineralization rate in the soils. In our experiment, the last application of nitrogen fertilizers was at onset of flowering and thus, plant growth under low nitrogen treatment obviously suffered from nitrogen deficiency during the grain filling period. There was a negative correlation between 1000-seed weight and number of seeds per pod ($r^2 = -0.12^{ns}$). It can be expected that the increase in seed number was parallel to the decrease in seed weight due to limitations in assimilate supply. As a result, those treatments with the highest seed numbers per pod produced the lowest 1000-seed weight (Table 4).

Harvest index

Harvest index (HI) was remarkably influenced by treatments. Increasing nitrogen rate from 90 to 180 kg N ha^{-1} significantly increased HI. Nonetheless, the highest

level of nitrogen (270 kg N ha^{-1}) led to lower HI. It seems that increasing nitrogen to 270 kg N ha^{-1} has decreased assimilates portioning to the seeds through increasing vegetative growth. On the other hand, high nitrogen availability may shift the balance between vegetative and reproductive growth toward excessive vegetative development, which may results in reduced yields (Fritschi et al. 2003). The highest HI was obtained in plants treated with $9 \text{ t zeolite ha}^{-1}$ and 180 and 270 kg N ha^{-1} (Table 5). Presumably, the slow release of nitrogen by zeolite provides a balance between vegetative and reproductive growth. Information regarding the effect of zeolite on crop growth and HI is scarce. There was also a positive correlation ($r^2 = 0.79^{**}$) between seed yield and HI. According to Diepenbrock (2000), for a given level of aboveground biomass, a greater HI represents a higher seed yield.

Protein content

The lowest (14.01%) and highest (26.5%) protein contents were obtained with treatments N_0Z_0 and N_{270}Z_9 , respectively (Table 5). The increase in both nitrogen and zeolite application rates, increased seed protein content. Numerous authors have emphasized a direct relationship between nitrogen application and seed protein percentage (Rathke et al., 2005; Kutcher et al., 2005). As a result, zeolite application increased seed protein via improving nitrogen availability at grain-filling stage. Nitrogen availability at an interval between pod setting stage and physiological maturity plays an important role on seed quality.

Oil content

Seed oil content was reduced with increased nitrogen and zeolite application rates (Table 5). The highest and lowest oil contents were obtained with treatments N_0Z_0 and N_{270}Z_9 , respectively. This result is supported by other researchers who found that nitrogen application decreases seed oil content at grain-filling stage. Scott et al. (1973) stated that the longer pod-development phase due to nitrogen fertilizer may increase the number of seeds that are fully mature and have lower oil content. Delayed maturity due to nitrogen application was considered as a probable reason for the reduction in canola seed oil content (Jackson 2000). By contrast, Holmes (1980) reported that a better supply of nitrogen increases the formation of nitrogen-containing protein precursors. Thus, protein formation competes more strongly for photosynthates, leading to fewer carbohydrates being involved in lipid biosynthesis. Likewise, Rathke et al. (2005) linked this fact to the reduced availability of carbohydrates for oil synthesis at high nitrogen rates. It was observed that a reduction in seed oil content due to high rates of nitrogen fertilizer is not consistent with findings of Jackson (2000). Jackson believed that the reduction in seed oil percentage by nitrogen is due to a delay in the onset of seed filling and maturation. However, in the our experiment, the 1000-seed weight increased with increasing nitrogen and zeolite rates, and N had no effect on the timing of canola phenological stages. Hocking et al. (2002) agree with our results.

In general, there was a negative correlation between oil and protein content, as stated by Rathke et al. (2005) and Hao et al. (2004). Such response could be explained through competition for carbohydrate metabolism. The synthesis of both fatty acids and amino acids requires carbohydrates as the base compound. Because the carbohydrate content of proteins is lower than that of oils (Lambers and Poorter

Table 5. Effect of nitrogen and zeolite application rates on harvest index, protein and oil content, leached nitrate, nitrogen efficiency ratio, nitrogen-use efficiency and nitrogen-uptake efficiency.

Nitrogen (kg ha ⁻¹)	Zeolite (t ha ⁻¹)	Harvest index (%)	Protein (%)	Oil (%)	Leached nitrate (kg ha ⁻¹)	Nitrogen efficiency ratio (kg kg ⁻¹)	Nitrogen-use efficiency (kg kg ⁻¹)	Nitrogen-uptake efficiency (kg kg ⁻¹)
0	0	19.66	14.01	48.97	12.43	46.03	—	—
90	0	13.83	18.55	48.94	26.86	36.76	17.43	0.761
180	0	25.30	19.90	47.76	63.89	32.91	10.06	0.470
270	0	25.13	21.17	45.87	142.72	31.14	7.02	0.353
90	3	23.46	18.16	49.13	24.26	36.63	17.02	0.774
180	3	25.86	20.43	47.95	57.74	33.26	10.31	0.483
270	3	25.36	21.77	46.10	126.59	31.8	7.22	0.373
90	6	23.00	20.02	48.61	21.58	36.75	16.69	0.782
180	6	25.70	22.35	46.67	48.92	32.78	10.57	0.540
270	6	24.96	23.29	44.73	105.88	28.7	7.61	0.461
90	9	23.36d	20.23	48.37	19.24	35.49	18.19	0.761
180	9	27.86	23.17	46.14	41.98	31.21	12.37	0.619
270	9	27.83	26.50	44.57	90.35	28.34	9.08	0.542
Mean		24.72	20.73	47.21	60.19	33.98	11.96	0.586
p-value		0.001	0.002	0.001	0.001	0.01	0.01	0.01
LSD		1.77	4.48	1.54	11.03	2.16	2.35	0.098
SE		0.36	0.58	0.29	6.81	0.9253	0.7490	0.0329
Nitrogen application rate (kg ha ⁻¹)								
90		23.41	19.24	48.76	13.06	36.41	17.33	0.7980
180		26.18	21.46	47.13	30.19	32.54	10.83	0.5280
270		25.82	23.18	45.32	66.13	29.99	7.73	0.4320
p-value		0.001	0.007	0.001	0.001	0.001	0.001	0.001
LSD		0.92	2.34	0.78	3.22	1.1	1.17	0.049
Linear		**	**	**	**	**	**	**
Quadratic		**	ns	ns	**	ns	**	**

(continued)

Table 5. (Continued).

Nitrogen (kg ha ⁻¹)	Zeolite (t ha ⁻¹)	Harvest index (%)	Protein (%)	Oil (%)	Leached nitrate (kg ha ⁻¹)	Nitrogen efficiency ratio (kg kg ⁻¹)	Nitrogen-use efficiency (kg kg ⁻¹)	Nitrogen-uptake efficiency (kg kg ⁻¹)
Zeolite application rate (t ha ⁻¹)								
0		24.75	19.87	47.52	77.82	33.60	11.50	0.5280
3		24.90	20.12	47.73	69.54	33.90	11.52	0.5430
6		24.55	21.88	46.67	58.79	32.74	11.62	0.5940
9		26.35	23.30	46.36	50.53	31.68	13.21	0.6780
<i>p</i> -value		0.007	0.050	0.012	0.001	0.006	0.0413	0.001
LSD		1.06	2.70	0.90	6.55	1.27	1.35	0.057
Linear		*	**	**	**	**	*	**
Quadratic		*	ns	ns	ns	ns	ns	ns
Significance								
N ₀ Z ₀ vs. N _x Z _x		**	**	**	**	**	—	—
N _x Z ₀ vs. N _x Z _x		Ns	ns	ns	**	ns	**	**
N _x Z ₀ vs. N _x Z ₉		**	ns	**	**	**	**	**
N × Z interaction								
<i>p</i> -value		0.2056	0.9430	0.9261	0.004	0.403	0.962	0.835

Note: Significant at the *0.05 and **0.01 probability levels. ns, not significant.

1992), increased nitrogen supply intensifies the synthesis of protein at the expense of fatty acids and thus reduces the oil content of the seed (Rathke et al. 2005).

Nitrate leaching

Experimental treatments had no significant effect on the ammonium concentration in drained water and drained ammonium (data not shown). In general, the ammonium concentration in drained water was $<1 \text{ mg l}^{-1}$. Because the experiment was performed in a sandy soil with high aeration, urea was quickly converted to ammonium and then to nitrate through nitrification, so the ammonium concentration was low in the soil and thus in drained water. The nitrate concentration in drained water was significantly affected by nitrogen and zeolite applications. Except for control (N_0Z_0), nitrate concentration in other treatments was $>10 \text{ mg l}^{-1}$, whereas in the control treatment it was 7.06 mg l^{-1} . The lowest ($12.43 \text{ kg nitrate ha}^{-1}$) and highest ($142.72 \text{ kg nitrate ha}^{-1}$) leached nitrate were obtained with treatment N_0Z_0 and N_{270}Z_0 , respectively. Losses of nitrate was 53, 47, 39 and 33% in N_{270}Z_0 , N_{270}Z_3 , N_{270}Z_6 and N_{270}Z_9 , respectively. Nitrate leaching was increased by increasing nitrogen application rates, but decreased by zeolite application (Table 5). An increase in nitrate leaching under irregular application of nitrogen fertilizer has been reported (Li et al. 2007). There were linear and quadratic relationships between nitrate leaching and nitrogen fertilizer levels. Such a relationship has also been reported by Fernandez-Escobar et al. (2004). In our experiment, it was found that application of $9 \text{ t zeolite ha}^{-1}$ severely decreased nitrate leaching compared with other application rates. This could be attributed to the unique physicochemical characteristics of mineral zeolite. The inner channels of clinoptilolite are large enough to fix cations such as NH_4^+ . Moreover, nitrifying bacteria were not able to stay on this product (He et al. 2002). Therefore, clinoptilolite may absorb the ammonium derived from urea applied in sandy soils and decrease the exchange rate of NH_4^+ with NO_3^- , which results in reduced N losses.

Nitrogen efficiency ratio (NER)

The highest (46.03 kg kg^{-1}) and lowest (28.43 kg kg^{-1}) NER values were obtained in control and N_{270}Z_9 , respectively. Additionally, more nitrogen and zeolite reduced NER in such a manner that the NER of experimental units fertilized with 90, 180 and 270 kg N ha^{-1} were 36.41, 32.54 and 29.99 kg kg^{-1} , respectively (Table 5). This shows that with increasing N uptake by canola seeds (under high nitrogen and zeolite), the efficiency of each nitrogen unit in producing grain yield is decreased.

Nitrogen-use efficiency (NUE)

Mean comparisons showed that 1 kg of nitrogen applied in treatments N_{90}Z_0 , N_{90}Z_9 , N_{180}Z_9 , N_{180}Z_0 , N_{270}Z_9 and N_{270}Z_0 resulted in 17.43, 18.19, 10.06, 12.37, 7.02 and $9.08 \text{ kg canola grain m}^{-2}$, respectively. Totally, NUE was decreased as the nitrogen application rate increased (Table 5). Similar results have been reported in wheat (Lopez-Bellido et al. 2005) and winter oilseed rape (Hocking et al. 2002; Svecnjak and Rengel 2006). Raun and Johnson (1999) also suggested nitrogen loss due to leaching as a main reason for low NUE under high nitrogen fertilizer

applications. Regardless of nitrogen rates (90, 180 and 270 kg N ha⁻¹), application of 9 t zeolite ha⁻¹ showed higher NUE than other zeolite rates. NUE in N₉₀Z₉, N₁₈₀Z₉ and N₂₇₀Z₉ was 4, 23 and 29% higher than in N₉₀Z₀, N₁₈₀Z₀ and N₂₇₀Z₀, respectively. As concluded previously, the important role of natural zeolite in reducing nitrogen leaching provides an opportunity for the crop to uptake more nitrogen and thus increases its grain yield. These could be related to enhanced NUE at the presence of zeolite. Rehakova et al. (2004) have also described the positive effect of zeolite on chemical fertilizer efficiency. Mean NUE in our experiment was 11.96 kg kg⁻¹, which is comparable with the values reported by Hocking et al. (2002) and Svecnjak and Rengel (2006).

Nitrogen-uptake efficiency (NUpE)

Application of more nitrogen fertilizer reduced NUpE (Table 5). NUpE of treatments received 90, 180 and 270 kg N ha⁻¹ was 0.811, 0.528 and 0.432 kg kg⁻¹, respectively. Fan et al. (2004) also found a similar response. Application of 9 t zeolite ha⁻¹ in plots treated with 90, 180 and 270 kg N ha⁻¹ resulted in 14, 30 and 54% increase in NUpE compared with zeolite-free treatment (Table 5). Rathke et al. (2006) stated that NUpE has a direct and high relationship with growth, development and biological activity of the crop root system. Rehakova et al. (2004) and Murphy et al. (2005) also stated that the physicochemical characteristics of clinoptilolite zeolite in the rhizosphere result in significant increases in plant biomass and root system activity. They attributed this effect to a better nutrient balance in the rhizosphere. This may explain the higher NUpE observed in this study under zeolite application.

Conclusion

Canola production in sandy soils might be considerably restricted as a result of low CEC and an increased risk of nitrogen leaching in irrigated lands or during the rainy season. In this study, incorporation of natural zeolite into a sandy soil decreased nitrate leaching and nitrogen efficiency ratio, and increased nitrogen-use efficiency and nitrogen-uptake efficiency. It was found that application of soil amendments such as zeolite improved soil physical properties. As a result, zeolite increased water-retention capacity and CEC, and thus nitrogen availability to the plants. However, from our results we conclude that reduction in nitrogen leaching is associated with a decrease in nitrogen fertilizer application. The results also indicated that zeolite caused an increase in canola yield. Thus, our hypothesis can be accepted and we conclude that zeolite application increases nitrogen-use efficiency and canola yield by avoiding nitrogen leaching and improving soil physical properties. Our results also indicated that amending soil with zeolite may be a beneficial approach for decreasing chemical fertilizer application rates and developing sustainable agriculture.

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