Soil & Tillage Research 126 (2013) 193–202

Contents lists available at SciVerse ScienceDirect

Soil & Tillage Research

journal homepage: www.elsevier.com/locate/still

Zeolite-amended cattle manure effects on sunflower yield, seed quality, water use efficiency and nutrient leaching

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ARTICLE INFO

Article history:
Received 22 February 2012
Received in revised form 1 August 2012
Accepted 4 August 2012

Keywords:
Composted manure
Irrigation regimes
Nutrient leaching
Sandy soil
Sunflower yield
Zeolite

ABSTRACT

Innovative strategies are needed to improve water and nutrient use efficiencies for sustainable production in sandy soils. Our objective was to determine the effects of applying cattle manure combined with zeolite and chemical fertilizer on (1) sunflower (*Helianthus annuus* L.) yield and quality and (2) nutrient leaching under two irrigation regimes on a sandy soil in a semi-arid region of Iran. The experiment was carried out using a randomized complete-block design, with a split-plot arrangement of treatments and four replications. Irrigation regime (I_1: full irrigation and I_2: limited irrigation) provided the whole-plot treatments with five fertilization strategies (F1: urea, F2: urea + composted manure (CM) with 0% (w/w) zeolite, F3: urea + CM with 7% zeolite, F4: urea + CM with 14% zeolite and F5: urea + CM with 21% zeolite) providing the sub-plots. Our results showed that limited irrigation (I_2) significantly decreased dry matter yield by 10% in 2008 and 9% in 2009. Dry matter and seed yield were considerably improved by the application of manure + zeolite in both years, but the impact of their application was greater in the second year than in the first. In both years, the maximum seed protein content was achieved with the F_5 treatment, while minimum seed protein content was observed in the F_2 and F_1 treatments for 2008 and 2009, respectively. Maximum irrigation water productivity was found with the I_2F_5 treatment combination in 2009 (0.81 kg m^{-3}), while the minimum value was found for the I_1F_1 combination in 2008 (0.48 kg m^{-3}). The highest and lowest rates of nitrate leaching were obtained from the I_1F_1 (36 kg ha^{-1}) and I_2F_5 (11 kg ha^{-1}) treatment combinations, respectively. Fertilizing only with urea (F_1) resulted in the highest nitrate leaching across both irrigation regimes, while the integrated treatments (F_2, F_3, F_4 and F_5) significantly decreased nitrate leaching, compared to the F_1 treatment, particularly with full irrigation (I_1). Addition of zeolite to the CM also decreased P leaching but not as much as for nitrate leaching. We concluded that amending soil with manure and zeolite can be a beneficial approach for decreasing chemical fertilizer application rates and improving the sustainability of agricultural systems.

1. Introduction

Modern farming practices impact soil and water quality so recent research has focused on management options for reducing nutrient loss, improving soil quality and increasing crop yield (Edmeades, 2003). Alternative management systems, such as organic and integrated farming, are being promoted because they are perceived to be more environmentally benign and to enhance soil and water quality relative to conventional practices (Reganold, 1995).

Sunflower is commonly grown on sandy soils in Iran. These soils provide ideal physical properties for sunflower growth (such as minimum compaction tendency and good aeration), but they have limited capacity to retain water and nutrients and are also prone to leaching of water-soluble nutrients such as N. Farmers cultivating these soils usually irrigate with large amounts of water and apply large amounts of fertilizer, especially N, to obtain high yields (Chen, 2003). This can result in substantial nutrient leaching so improved nutrient management strategies are needed to optimize yield while minimizing the potential for environmental pollution.

Historically, organic materials such as manure have been mixed with sandy soil to improve water and nutrient retention (Bigelow et al., 2004). Organic matter, especially cattle manure, affects crop growth and yield directly by supplying nutrients and indirectly by modifying soil physical properties that can improve the root

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http://dx.doi.org/10.1016/j.still.2012.08.002

environment and stimulate plant growth (Bandyopadhyay et al., 2010). Cattle manure is generally used in two forms: fresh or composted. Fresh manure has lower C:N ratio than composted manure, but it is more difficult to store and transport if it is not from on-farm livestock. There is evidence that at least 50% of N in manure is lost in storage and transport, and another 25% is lost after application (Dawson et al., 2008). Manure composting, by contrast, is a useful method of producing a stabilized product that can be stored or spread with little odor or fly breeding potential. The other advantages of composting include killing pathogens and weed seeds and improving manure handling by reducing its volume and weight (Eghball, 2002). However, composting has some disadvantages, including loss of nutrients and C during the composting process (Eghball et al., 1997). Better procedures are needed to stabilize manure before and after its application on farms, especially sandy farms. A variety of additives have been investigated for application to fresh manure; among them is natural zeolite.

Zeolites are crystalline, hydrated aluminosilicates that have three-dimensional crystal structures (Rehakova et al., 2004). They are characterized by an ability to lose and gain water reversibly and to exchange their constituent elements without a major change of structure (Leggo et al., 2006; Ok et al., 2003). Clinoptilolite is not the most well known of the zeolites, but it is one of the most useful natural zeolites because of its high cation exchange capacity (200–300 meq 100^{-1} g) (Leggo et al., 2006), selective absorption and structure stability over the long term (Baerlocher et al., 2001). Extensive deposits of clinoptilolite are found in the western United States, Bulgaria, Hungary, Japan, Australia, China and Iran (Mumpton, 1999). In Iran zeolite cost is approximately 2.5 cent per kg so application of zeolite could be economical. The size of the channels in zeolite control the size of the molecules or ions that can pass through them, and therefore, a zeolite such as clinoptilolite can act as a chemical sieve, allowing some ions to pass through while blocking others (Baerlocher et al., 2001). Additionally, clinoptilolite zeolite is a stable mineral in soil and shows good stability against weathering, impact and abrasion tests (Ok et al., 2003).

Sunflower is one of the most important oil crops in the world. Its growth is favored because it has high climate adoption capability, suitability for mechanization and low labor needs. Water and N are the most important inputs for sunflower production, and it is essential to understand the impacts of N management under different irrigation regimes. This study was conducted because there has been no published work on the effect of applying to soil cattle manure combined with zeolite and chemical fertilizer. Effects on sunflower yield, seed quality and nutrient leaching were evaluated for five fertilizer treatments and two irrigation regimes.

2. Materials and methods

2.1. Experiment location and general methodology

The experiment was conducted on sandy loam soil during the 2008 and 2009 growing seasons at the research farm of Tarbiat Modares University, Tehran, Iran (35°41′N, 51°19′E and 1215 masl). The region is characterized as semi-arid, with mean annual precipitation of 298 mm, which mostly falls during the autumn and winter months. Daily meteorological data on precipitation and air temperature were obtained from the nearest weather station (500 m from the experimental site) (Fig. 1). Before planting, several soil samples were taken at depths of 0–30 and 30–60 cm, composite samples were collected, air-dried, crushed, and tested for physical and chemical properties (Table 1).

2.2. Manure and zeolite composting

Three months before field preparation, fresh dairy cattle manure and zeolite were transported to the study site. Zeolite was sourced from a quarry in the city of Mianeh in northwest Iran and was composed of about 90% clinoptilolite. The remainder consisted of volcanic glass, clay minerals, quartz and feldspar. X-ray spectrophotometer analysis (dispersive spectra) showed that the clinoptilolite of Mianeh was of the K–Ca type, with a low content of Na ions. Zeolite analysis indicated a cation exchange capacity (CEC) of 200 meq 100^{-1} g and the other chemical properties of zeolite was as follows: silicon dioxide (SiO_2), 65%; aluminum oxide (AL_2O_3), 12%; sodium oxide (Na_2O), 1%; potassium oxide (K_2O), 3% and calcium oxide (CaO), 2.5%. Each year, the chemical properties of the cattle manure were analyzed before composting (Table 2). The analyses showed that fresh cattle manure had 1.28 and 1.42% total N by weight in 2008 and 2009, respectively. During composting, a known dry weight of manure was stored in four rows, each 8 m long, 1 m wide and 0.8 m high. Zeolite was then mixed into three of the manure rows in

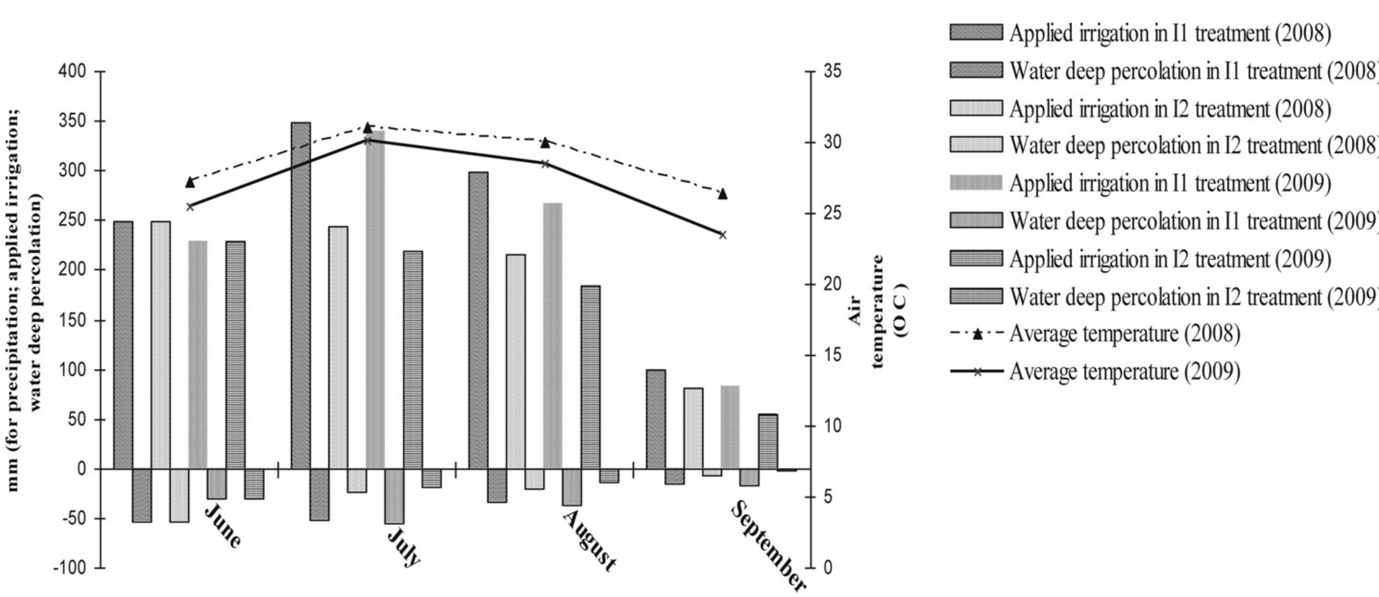

Fig. 1. Applied irrigation and water deep percolation during the first and second years of experiment and average monthly temperature of the growth seasons (2008 and 2009).

Table 1
Soil physiochemical properties.

Properties	Depth (cm)			
	0–30		30–60	
	2008	2009	2008	2009
Organic matter (%)	0.5	0.7	0.4	0.5
pH (water 1:2 ratio)	6.9	7.4	6.5	7.00
Sand (%)	68	57	59	52
Silt (%)	18	22	29	30
Clay (%)	14	21	12	18
[c]EC (dS m^{-1})	1.3	1.6	1.3	1.5
N (%)	0.07	0.15	0.09	0.1
P (mg kg^{-1})	10.5	12	n.d[a]	n.d
K (mg kg^{-1})	320	345	n.d	n.d
Fe (mg kg^{-1})	7.9	7.2	n.d	n.d
Zn (mg kg^{-1})	1.5	0.9	n.d	n.d
$CaCo_3$ (%)	4.6	5.7	n.d	n.d
CEC[b] (meq 100^{-1} g)	5.4	6.9	n.d	n.d

[a] Not determined.
[b] Cation exchange capacity.
[c] EC = Electrical conductivity.

proportions of 7%, 14% and 21% by weight of the manure (w/w). The heaps were covered with straw and stubble to protect them from direct sunlight. Temperature and moisture were monitored daily while the manure was aerobically composted for 85 days.

2.3. Composting sampling and analysis

After composting, 1 kg samples were collected after mixing of each heap from 5 to 10 points within each manure heap. Samples were placed on clean plastic boards, broken up and mixed thoroughly; after which, subsamples of about 0.5 kg were taken to determine water content. The reminder was air-dried to determine N availability (Table 3). Based on the known N requirements of sunflowers (130 kg N ha^{-1}), 50 kg N was supplied by composted manure and 80 kg N was supplied using urea fertilizer.

2.4. Land preparation and introduction of treatments

Sunflower was planted in different sections of the field each year following wheat (*Triticum aestivum* L.) in 2008 and field corn (*Zea mays* L.) in 2009. The field was prepared by shallow plowing, followed by disking in late May. Weeds were controlled by applying trifluralin (3.5 l ha^{-1}) and then incorporating it into the soil using a disk. Each experimental unit was 10 m long and consisted of 10 rows spaced 0.5 m apart. There were 2 m gaps between the blocks, and a 1 m alley was established between each plot to prevent lateral water movement and other interferences. A polyethylene pipeline and a counter were installed to control irrigation.

The experiment was conducted using a randomized complete-block design with a split-plot arrangement of treatments and four replicates. The main plot treatment was irrigation, which was defined with respect to water deficit (I_1: irrigation was initiated after 40% of available water was used (full irrigation), I_2: irrigation was initiated after using 80% of available water was used (limited irrigation)). The fertilizer subplot treatments were F_1: 130 kg ha^{-1} N as urea, F_2: 80 kg ha^{-1} N as urea + 50 kg ha^{-1} N as cattle manure, F_3: 80 kg ha^{-1} N as urea + 50 kg ha^{-1} N as cattle manure plus 7% zeolite, F_4: 80 kg ha^{-1} N as urea + 50 kg ha^{-1} N as cattle manure plus 14% zeolite, F_5: 80 kg ha^{-1} N as urea + 50 kg ha^{-1} N as cattle manure plus 21% zeolite.

2.5. Establishing of the treatments and planting

Before planting, composted manure (treatments F_2, F_3, F_4 and F_5) was applied by hand and incorporated into the top 15 cm of the soil. Chemical N fertilizer was divided into two equal amounts and applied at two stages, sowing and flowering (the latter is the R-2 stage described by Schneiter and Miller, 1981). Potassium and phosphorus fertilizers were not applied in either year because soil tests showed they were already present in adequate amounts.

An early maturing sunflower cultivar ('Blizar') was sown by hand at depths of 5 cm on 9 June 2008 and 3 June 2009. To ensure good emergence, the experimental plots were over-seeded and then thinned (to 30 cm spacing) to achieve the recommended plant density of 66,000 plants ha^{-1} at the two-leaf stage. Immediately after sowing, the soil was irrigated. The irrigation cycle of each plot was closed to avoid runoff. Irrigation scheduling was determined according to daily changes of soil water content (ΔSW) at the depth of root development. A deficit approach was used to estimate irrigation requirements: soil water content at field capacity (FC) was defined as no water deficit. Available water was determined by the difference between the water content at field capacity and permanent wilting point (PWP). Until the blooming stage (between the R-1 and R-2 stages described by Schneiter and Miller, 1981), irrigation was initiated similarly in all plots when 40% of available water had been consumed at the depth of root development. After the blooming stage, plots received different irrigation treatments.

Time-domain reflectometry (TDR) probes with tube access (TRIME-FM, England) were used to measure soil water content (θ_v) in experimental plots at 0–80 cm soil depth (at 0.2 m intervals). Data on soil volumetric water content were collected daily during the growing season. Prior to seed sowing, at the same time as TDR tube access probe installation, soil water sampler tubes (Model 1900, Soil Moisture Equipment Co.) were inserted into vertical holes of 5–6 cm in diameter and 80 cm depth created with a hand auger in the middle of each plot. To avoid possible contamination, the ceramic caps of the soil water sampler tubes were washed before insertion, and to facilitate good contact between the ceramic cap and the soil, the gaps were filled with soft soil.

Table 2
Fresh manure properties.

EC (dS m^{-1})		N (%)		P (%)		K (%)		Na (%)		OC (%)		OM (%)	
2008	2009	2008	2009	2008	2009	2008	2009	2008	2009	2008	2009	2008	2009
22.2	23.7	1.3	1.4	0.6	0.6	2.5	2.6	1.2	1.2	29.7	30.2	50.1	52.1

SC (%)		C:N		pH		Fe (mg kg^{-1})		Cu (mg kg^{-1})		Zn (mg kg^{-1})		Mn (mg kg^{-1})	
2008	2009	2008	2009	2008	2009	2008	2009	2008	2009	2008	2009	2008	2009
220	245	23.2	21.3	9.2	9.0	6870	7210	23.5	25.5	110	121	301	295

Abbreviations: EC, electrical conductivity; OC, organic carbon, OM, organic matter; SC, saturated capacity.

Table 3
Analysis of cattle manure after composting.

Parameters	Year	Treatments			
		F_2 (Z_0)	F_3 (Z_7)	F_4 (Z_{14})	F_5 (Z_{21})
Moisture (%)	2008	9.2	12.1	11.6	13.4
	2009	10.1	11.0	14.5	13.8
Nitrogen wasting during composting (%)	2008	40	31	20	15
	2009	47	36	26	12
Total N after composting (%)	2008	0.77	0.88	1.02	1.09
	2009	0.75	0.90	1.05	1.25
Organic nitrogen (%)	2008	0.67	0.75	0.83	0.87
	2009	0.65	0.75	0.86	1.01
NH_4^+ (%)	2008	0.08	0.12	0.19	0.21
	2009	0.10	0.14	0.18	0.23
NO_3^- (%)	2008	0.007	0.008	0.008	0.005
	2009	0.003	0.013	0.010	0.006
Available nitrogen[a] (%)	2008	0.25	0.30	0.38	0.42
	2009	0.26	0.32	0.38	0.47
Applied composted manure (t ha^{-1})	2008	20	16	13	12
	2009	20	15.5	13	11
Applied zeolite (kg ha^{-1})	2008	–	1120	1820	2520
	2009	–	1080	1820	2310

F2, urea + composted manure (CM) with 0% (w/w) zeolite; F3, urea + CM with 7% zeolite; F4, urea + CM with 14% zeolite; F5, urea + CM with 21% zeolite.
[a] Available Nitrogen = 95% of NH_4^+ + 25% of NO_3^- (Tarkalson et al., 2006).

2.6. Soil water sampling and analysis

Determining solute-leaching losses required two sets of information: the quantity of the drainage flux and the solute concentration of the drainage solution. A portable vacuum pump (Model 2005 G2, Soil Moisture Equipment Co.) was used to apply −30 kPa tension for collecting water samples every 4–6 days or when drainage was expected to have occurred, such as after rain or irrigation (when soil water content was likely to exceed field capacity). Water samples were taken from the soil water sampler tubes using a thin collection vessel, a vacuum Erlenmeyer flask and a vacuum hand pump. The samples were acidified with sulfuric acid (1 ml l^{-1}) and stored in a refrigerator. Water samples were analyzed via spectrophotometry (Model dr/2500, Hach Co.) for NO_3^- and P concentrations using the cadmium and ascorbic acid methods, respectively. For daily measurements of deep percolation, the water balance equation (Errebhi et al., 1998) was used (Eq. (1)):

$$\text{daily deep percolation} = P + I - \Delta SW - ET_C - R \tag{1}$$

where P is precipitation (mm), I is irrigation water applied (mm), ΔSW is the daily change in soil water content (mm) at the depth of root development (measured by TDR), ET_C is crop evapotranspiration (mm) and R is runoff (mm). There was no runoff because irrigation cycles in each plot were closed. Percolation occurs whenever the sum ($P + I$) is higher than (ΔSW + ET_C) (Vazquez et al., 2005). Water input from irrigation and rainfall were measured at the experiment site.

Crop evapotranspiration was calculated daily using Eq. (2):

$$ET_C = ET_0 \times K_C \tag{2}$$

where ET_0 refers to evapotranspiration calculated by the FAO-Penman–Monteith method (Allen et al., 1998), which depends on daily weather conditions at the site, and K_C is the crop coefficient. The values of K_C calculated by the FAO (Doorenbos and Pruitt, 1977; Doorenbos and Kassam, 1979) were used for each sunflower growth stage. The initial water storage was equal to the soil water holding capacity to 80 cm depth (before sowing, when the soil was fully saturated), and subsequent changes in water storage (ΔSW) were determined on a daily basis. In I_2 irrigation treatments (water deficit), ET_C was adjusted and calculated by Eq. (3) (Chow et al., 1988; Allen et al., 1998):

$$ET_{C-\text{adj}} = K_S \times K_C \times ET_0 \tag{3}$$

where K_C and ET_0 are the same as in Eq. (2) and K_S is a correction coefficient (with no dimension) for calculating ET_C under water stress conditions. K_S was calculated by Eq. (4):

$$\frac{\text{TAW} - D_r}{\text{TAW} - \text{RAW}} KS = 1 \quad \text{if} \;\; D_r < \text{RAW} \tag{4}$$

where TAW is total available water in the root zone (mm, difference between the water content at FC and PWP), D_r is the amount of water depletion from root zone (mm, monitored on a daily basis by TDR) and RAW is readily available water in root zone (mm, calculated by multiplying TAW by MAD (management allowed depletion), which was defined as an 80% depletion of available soil water in the I_2 irrigation treatment).

The mass of NO_3^- and P in leachate was determined as follows:

$$NO_3^- \text{mass}(\text{kg ha}^{-1}) = \text{NC} \times \text{WDP} \times 0.01 \tag{5}$$

$$\text{P mass}(\text{kg ha}^{-1}) = \text{PC} \times \text{WDP} \times 0.01 \tag{6}$$

where NC and PC are the concentrations of nitrate and phosphorus in leachate (mg L^{-1}), WDP is the amount of water deep percolation (mm) and 0.01 is the conversion factor from mg L^{-1} to kg ha^{-1}.

2.7. Plant and soil measurements

At the seed filling stage, leaf samples were taken to determine the N content of leaves using a Kjeltec Auto 1030 Analyser (Tecator, Sweden). Leaf area index (LAI) and leaf chlorophyll content (SPAD value) were measured with a leaf area meter (Delta-T area meter; Delta-T Devices Ltd., Cambridge, UK) and a chlorophyll meter (SPAD-502 Minolta, Japan), respectively. Four weeks after the

Table 4
Analysis of variance (mean squares) for the effects of different sunflower parameters (year, irrigation and fertilizer treatments) on the measured traits.

Source of variance	df	SPAD[a]	L.N.C[a]	LAI[a]	R.W.C	D.M.Y	S.Y	S.O.C
Year	1	130.86*	0.81*	4.154**	135.64**	2,942,442.18**	1,129,574.21**	14.11 NS
Replication × year	6	5.691	0.051	0.045	2.898	54,501.42	83,224.18	5.11
Irrigation (I)	1	164.96*	1.66**	1.937**	1992.30**	5,131,756.74**	4,231,402.02**	276.02**
Year × I	1	1.128 NS	0.002 NS	0.007 NS	10.738 NS	10,543.23 NS	162,243.09 NS	26.91**
Replication × year × I	6	21.743	0.11	0.054	8.955	76,540.80	21,790.07	5.24
Fertilizer treatments (F)	4	51.221**	0.647**	0.627**	106.66**	1,692,878.89**	1,087,266.44**	7.35 NS
Year × F	4	4.229 NS	0.047 NS	0.090 NS	7.966 NS	427,089.60**	45,031.41NS	1.41 NS
I × F	4	1.431 NS	0.035 NS	0.015 NS	3.716 NS	25,987.46 NS	30,347.34 NS	1.94 NS
Error	52	5.50	0.046	0.044	8.83	92,421	66,275	3.35
C.V. (%)		6.40	7.77	10.84	4.40	6.05	13.21	4.09
Source of variance	df	S.Pr.C	S.P.C	S.K.C	I.W.P	C.E.C	N.L	P.L
Year	1	1.22 NS	0.038**	0.080**	0.251**	21.16**	1575.87**	70.38**
Replication × year	6	1.28	0.002	0.002	0.0007	0.054	7.19	1.37
Irrigation (I)	1	20.91*	0.177**	0.079**	0.189**	0.120 NS	5025.69**	658.08**
Year × I	1	0.136 NS	0.004 NS	0.009*	0.013**	0.011 NS	16.69 NS	27.08**
Replication × Year × I	6	2.21	0.001	0.001	0.001	0.213	10.29	0.704
Fertilizer treatments (F)	4	10.80**	0.117**	0.083**	0.026**	11.88**	186.71**	270.17**
Year × F	4	3.41 NS	0.0003 NS	0.002 NS	0.007**	0.69**	30.96 NS	7.96 NS
I × F	4	0.55 NS	0.0003 NS	0.0003 NS	0.001 NS	0.005 NS	46.42*	41.28**
Error	52	1.36	0.002	0.001	0.001	0.144	14.06	3.67
C.V. (%)		5.90	6.25	9.08	6.50	4.98	17.93	25.17

L.A.I, Leaf Area Index; R.W.C, relative water content; D.M.Y, dry matter yield; S.Y, seed yield; S.O.C, seed oil content; S.Pr.C, seed protein content; S.P.C, seed P content; S.K.C, seed K content; I.W.P, irrigation water productivity; C.E.C, soil cation exchange capacity; N.L, nitrate leaching; P.L, phosphorus leaching; NS, not significant at the 0.05 or 0.01 probability levels; L.N.C, Leaf N concentration.
[a] Measured at grain filling stage.
* Significant at the 0.05 probability levels.
** Significant at the 0.01 probability levels.

onset of irrigation regimes, RWC (relative water content) of leaves was calculated. To determine RWC, eight leaves from each plot were weighed (fresh weight, FW) immediately after being harvested from the plants. The same tissues were then placed in a vial of distilled water for 2 h at 25 °C, after which their turgid weights (TW) were measured. The samples were then dried in an oven at 110 °C for 24 h to obtain their dry weights (DW). Relative water contents were calculated with Eq. (7):

$$\frac{FW - DW}{TW - DW} \times 100 \tag{7}$$

To determine sunflower dry matter and seed yield, 10 m^2 of each plot was hand-harvested at the physiological maturity stage. The oil and protein percentages of the seeds were determined using an Inframatic 8620 (Percor, Germany). P concentration in seeds was measured calorimetrically (using a 6505 JenWay spectrophotometer), and K concentration in seeds was measured with flame photometry (using a JenWay PFP7 flame-photometer). Irrigation water productivity (IWP) was calculated as dry matter yield (kg ha^{-1}) divided by total seasonal applied irrigation water (m^3). After harvesting surface soil samples were collected with a hand auger from 0 to 30 cm depth at 5 locations per plot to determine cation exchange capacity (CEC). The CEC values were determined via an ammonium saturation method (Page et al., 1982).

2.8. Statistical analysis of data

All data were subjected to analysis of variance (ANOVA) using SAS software (SAS Institute, 2002). Bartlett's test showed homogeneity of variance in all traits in both years. When an *F*-test indicated statistical significance at $P < 0.01$ or $P < 0.05$, the

Table 5
Mean comparison of irrigation regimes and year main effect.

Treatments	Traits							
	SPAD[a]		L.N.C (%)[a]		LAI[a]		R.W.C (%)	
Main effect	2008	2009	2008	2009	2008	2009	2008	2009
Full irrigation (I_1)	36 a	39 a	2.8 a	3.0 a	1.9 a	2.3 a	71 a	73 a
Limited irrigation (I_2)	33 b	36 b	2.5 b	2.7 b	1.5 b	2.0 b	60 b	64 b
Year	35 b	37 a	2.7 b	2.8 a	1.7 b	2.2 a	66 b	68 a
Treatments	Traits							
	D.M.Y (kg ha^{-1})		S.Y (kg ha^{-1})		S.Pr.C (%)		N.L (kg ha^{-1})	
Main effect	2008	2009	2008	2009	2008	2009	2008	2009
Full irrigation (I_1)	5070 a	5480 a	2100 a	2250 a	19 b	19 b	32 a	24 a
Limited irrigation (I_2)	4590 b	4950 b	1550 b	1880 b	20 a	20 a	17 b	8 b
Year	4828 b	5212 a	1829 b	2067 a	19 a	19 a	25 a	16 b

I_1, irrigation after using 40% available water; I_2, irrigation after using 80% available water (water deficit). L.N.C, leaf N concentration; L.A.I, Leaf Area Index; R.W.C, relative water content; D.M.Y, dry matter yield; S.Y, seed yield; S.Pr.C, seed protein content; N.L, nitrate leaching.
Means within each column of each section (for irrigation effect) and each row of year effect followed by the same letter are not significantly different ($p \leq 0.05$).
[a] Measured at grain filling stage.

Table 6
Mean comparison of fertilizer treatments main effect.

Treatments	Traits							
	SPAD[a]		L.N.C[a] (%)		LAI[a]		R.W.C (%)	
Main effect	2008	2009	2008	2009	2008	2009	2008	2009
F1	32 b	36 c	2.4 c	2.6 d	1.4 d	1.8 c	61 b	64 b
F2	34 ab	36 c	2.6 bc	2.7 cd	1.6 bc	2.0 bc	66 a	70 a
F3	35 ab	37 bc	2.4 c	2.8 bc	1.6 c	2.2 ab	68 a	68 a
F4	36 a	39 ab	2.7 ab	3.0 ab	1.9 a	2.2 ab	67 a	69 a
F5	37 a	40 a	2.9 a	3.1 a	1.8ab	2.4 a	67 a	70 a

Treatments	Traits							
	S.Y ($kg\ ha^{-1}$)		S.Pr.C (%)		S.P.C (%)		S.K.C (%)	
Main effect	2008	2009	2008	2009	2008	2009	2008	2009
F1	1470 c	1760 c	19 bc	18 b	0.57 b	0.62 b	0.34 c	0.38 c
F2	1750 b	1880 c	18 c	19 ab	0.77 a	0.82 a	0.43 b	0.49 b
F3	1800 b	1970 bc	19 bc	20 a	0.77 a	0.81 a	0.46 ab	0.50 b
F4	2080 a	2280 ab	20 ab	19 b	0.77 a	0.80 a	0.47 ab	0.57 a
F5	2040 a	2440 a	21 a	20 a	0.76 a	0.81 a	0.50 a	0.59 a

F1: urea; F2: urea + composted manure (CM) with 0% (w/w) zeolite; F3: urea + CM with 7% (w/w) zeolite; F4: urea + CM with 14% (w/w) zeolite; F5: urea + CM with 21% (w/w) zeolite.
L.N.C, leaf N concentration; LAI, Leaf Area Index; R.W.C, relative water content; S.Y, seed yield; S.Pr.C, seed protein content; S.P.C, seed P content; S.K.C, seed K content. Means within each column of each section followed by the same letter are not significantly different ($p \leq 0.05$).
[a] Measured at grain filling stage.

protected least significant difference (protected LSD) was used to separate the means of main effect and the significant interaction effects were separated by slicing method.

3. Results and discussion

3.1. Weather conditions

Meteorological data showed that 2008 had higher mean temperature and lower precipitation than either 2009 or the long-term average (Fig. 1). Total irrigation in the I_1 and I_2 treatments in 2008 were 994 and 789 mm, respectively. In 2009 the amount of irrigation water was decreased to 919 and 687 mm for the I_1 and I_2 treatments, respectively, due to cold weather and high soil moisture retention capacity. For I_1, 16 and 15% of the applied water was lost from the root zone as drainage water in 2008 and 2009, respectively. In contrast, I_2 lost only 13 and 9% of the applied irrigation during 2008 and 2009, respectively.

Because sunflower plants have limited root expansion and minimal water uptake during early growth stages, maximum drainage was observed during June and July in both years (Fig. 1).

3.2. Analysis of variance

An analysis of variance showed that year, irrigation regime and fertilizer treatment, significantly affected all parameters except: (1) effect of year on seed oil and protein content; (2) effect of irrigation regime on soil CEC; and (3) effect of fertilizer treatments on seed oil content (Table 4). There was a significant year × irriga-irrigation regime interaction effect for seed oil content, seed potassium content and irrigation water productivity, and the year × fertilizer treatment interaction effect was significant for dry matter yield, irrigation water productivity and soil CEC (Table 4). Furthermore, the irrigation regime × fertilizer treatment interaction effect was significant only for nitrate and phosphorus leaching loss (Table 4). Interaction and main treatment effects are discussed below in the order of their statistical significance, which ranges from the highest-level interactions to the main effects of treatments.

3.3. SPAD value (Sv) and leaf N concentration (LNC)

Mean comparisons showed that Sv and LNC were lower in 2008 than in 2009 (Table 5) because of enhanced N leaching and reduced N availability in 2008. Low plant-available water in the I_2 irrigation treatment decreased Sv and LNC in both years (Table 5). Presumably, transpiration reduction due to water deficiency in the I_2 treatment reduced the mass flow of water through the soil under the I_2 water regime, consequently decreasing N absorption by plants.

Among fertilizer treatments, F_5 showed the maximum Sv and LNC in both years; however, F4 and F5 were not significantly different (Table 6). In both years, Sv and LNC were higher in all integrated treatments (F_2–F_5) than for the chemical treatments (F_1). The application of manure improves soil physical and chemical properties and increases root activity, leading to enhancement of plant N absorption. Furthermore, the unique mineral properties of clinoptilolite zeolites, including high CEC and high affinity for NH_4^+ (He et al., 2002), facilitated ammonium retention when zeolite was mixed with fresh manure. When the manure + zeolite mixture was applied to moist soil, the ammonium ions are gradually exchanged and oxidized by nitrifying bacteria. This significantly increased the soil N concentration and N uptake by plants.

3.4. Leaf Area Index (LAI) and relative water content (RWC)

The leaf area index rose by 29% in the second year in comparison with the first year presumably because of more favorable climatic conditions (Table 5). In both years, reduced water availability with the I_2 irrigation treatment caused LAI and RWC to decrease significantly (Table 5). One major reason for slow leaf expansion under conditions of water deficiency is reduction in leaf cell hydraulic conductivity, which in turn decreases water transport, and hinders cell enlargement and leaf development. A significant and direct correlation between RWC and LAI ($r^2_{\text{year}(1)} = 0.72^{***}$, $r^2_{\text{year}(2)} = 0.53^{*}$) supported this hypothesis.

In both years, treatment F_1 had the lowest LAI, being 23% lower than for F_4 (which had a maximum LAI in 2008) and 27% lower than for F_5 (which had a maximum LAI in 2009). This can be explained

Table 7
Mean comparison of interaction effects of year × fertilizer treatments.

Year × fertilizer treatments effect sliced by year for D.M.Y			Year × fertilizer treatments effect sliced by year for I.W.P			Year × fertilizer treatments effect sliced by year for C.E.C		
Year	Fertilizer treatments	D.M.Y (kg ha^{-1})	Year	Fertilizer treatments	I.W.P (kg m^{-3})	Year	Fertilizer treatments	C.E.C (meq 100 g soil^{-1})
2008	F1	4490 c	2008	F1	0.50 c	2008	F1	5.3 d
	F2	4720 bc		F2	0.53 bc		F2	7.1 c
	F3	4940 ab		F3	0.55 ab		F3	7.1 c
	F4	5060 a		F4	0.57 a		F4	7.6 b
	F5	4940 ab		F5	0.55 ab		F5	8.2 a
2009	F1	4660 d	2009	F1	0.58 d	2009	F1	7.0 c
	F2	5040 c		F2	0.64 c		F2	8.2 b
	F3	4980 c		F3	0.62 c		F3	8.2 b
	F4	5520 b		F4	0.69 b		F4	8.4 ab
	F5	5830 a		F5	0.73 a		F5	8.7 a

D.M.Y., dry matter yield; I.W.P, irrigation water productivity; C.E.C, soil cation exchange capacity.
F1, urea; F2, urea + composted manure (CM) with 0% (w/w) zeolite; F3, urea + CM with 7% (w/w) zeolite; F4, urea + CM with 14% (w/w) zeolite; F5, urea + CM with 21% (w/w) zeolite.
Means within each column of each section followed by the same letter are not significantly different ($p \leq 0.05$).

by the fact that leaf expansion is related to both N availability and water availability. Even with full irrigation (I_1), F_4 in 2008 and F_5 in 2009, improved soil physical characteristics and resulted in greater root distribution and penetration. Furthermore, LAI was enhanced by greater water and N uptake due to zeolite activity in the F_4 and F_5 treatments.

3.5. Dry matter yield (DMY) and seed yield (SY)

Results showed that limited irrigation in the I_2 treatment significantly decreased DMY by 10% in 2008 and 9% in 2009 when compared with I_1 (Table 5). As shown in Table 7, the F_5 fertilizer treatment in 2009 had the highest DMY (5828 kg ha^{-1}), whereas the F_1 treatment in 2008 had the lowest DMY (4488 kg ha^{-1}). In both years, the application of manure + zeolite considerably increased DMY, but the effect was stronger in 2009 (Table 7). In 2008, there was no significant DMY difference between the different zeolite treatments (F_3, F_4 and F_5), but in 2009, DMY was significantly higher for F_5 than for F_4 and F_3 (Table 7). Many researchers have reported that manure application has positive effects on the physicochemical properties of soil and improves crop yields (Bhattacharyya et al., 2008; Basso and Ritchie, 2005; Herenica et al., 2007). Additionally, it seems that adding zeolite to fresh manure prevents the N loss from the soil due to absorption and subsequent release of the N by the zeolite. In this way, composted manure can act as a slow-release fertilizer to supply N to the crop gradually. A direct relationship between N supply and crop dry matter has been reported by Hermanson et al. (2000). Thus, it is to be expected that that integrated treatments with zeolite (especially F_4 and F_5) will increase crop dry matter yield.

The I_1 treatment had a higher SY than did the I_2 treatment (Table 5). Low sunflower SY under limited irrigation could result from reduced head diameter and seed number per head. Although limited water application (I_2) led to optimum water use efficiency (data not shown), SY decreased by 23% and 21% as compared to the I_1 treatment, respectively. The results show the importance of improving sandy soils to achieve optimum yields in parallel with reduction of water use.

Among the fertilizer treatments in 2008, F_4 had the maximum SY, but in 2009 it was obtained with the F_5 treatment (Table 6). In 2008, F_4 had seed yields that were 19 and 41% higher than seed yields for F_2 and F_1, respectively. In 2009, SY in F_5 was 29 and 39% higher than for F_2 and F_1, respectively. It appears the SY increase for F4 and F5 treatments resulted from a proper balance between available soil N and plant N requirements. In early growth stages, during which the crop's nutrition requirements are low, soil N concentrations in the F_4 and F_5 treatments were lower than in F_1 (data not shown), but due to the gradual release of N from composted manure plus zeolite, N availability lasted longer in the F_4 and F_5 treatments and resulted in higher N availability during the reproductive stage. Leaf N concentration during early flowering and seed filling stages can serve as a useful metric for these evaluations. Our data showed that leaf N concentration in integrated treatments was no greater than in the chemical treatment in the early flowering stage (data not shown), but during seed-filling stage the highest leaf N concentrations were measured in the F_4 and F_5 treatments in both years (Table 6). Reductions in soil bulk density, increased in soil water retention capacity (data not shown) and enhanced of soil microbial activity (Bhattacharyya et al., 2008) due to application of manure can also account for SY increases.

Table 8
Mean comparison of interaction effects of year × irrigation regimes.

Year × irrigation regimes effect sliced by year for S.O.C			Year × irrigation regimes effect sliced by year for S.K.C			Year × irrigation regimes effect sliced by year for I.W.P			Year × irrigation regimes effect sliced by year for P.L		
Year	Irrigation regimes	S.O.C (%)	Year	Irrigation regimes	S.K.C (%)	Year	Irrigation regimes	I.W.P (kg m^{-3})	Year	Irrigation regimes	P.L (kg ha^{-1})
2008	Full	46 a	2008	Full	0.48 a	2008	Full	0.51 b	2008	Full	8.9 a
	Limited	41 b		Limited	0.40 b		Limited	0.58 a		Limited	4.3 b
2009	Full	46 a	2009	Full	0.53 a	2009	Full	0.59 b	2009	Full	12.0 a
	Limited	43 b		Limited	0.48 b		Limited	0.71 a		Limited	5.1 b

S.O.C, seed oil content; S.K.C, seed P content; I.W.P, irrigation water productivity; P.L, P leaching. Full irrigation, irrigation after using 40% available water; limited irrigation, irrigation after using 80% available water (water deficit).
Means within each column of each section followed by the same letter are not significantly different ($p \leq 0.05$).

3.6. Seed oil content (SOC) and seed protein content (SPrC)

Seed oil content (SOC) was significantly affected by the interaction of year × irrigation regime (Table 4). Table 8 shows that water deficiency (I_2) reduced SOC in both years, but the difference between I_2 and I_1 was 11% in 2008 compared to 5% in 2009. Studies suggested that abscisic acid produced in leaves of stressed plants is translocated to the seeds and thus contributes to the decline in the SOC (Unger and Paul, 1982; Connor and Sadras, 1992). Results showed that the I_2 treatment increased SPrC as compared to the I_1 treatment (Table 5). A reduction in the seed-filling period due to water deficiency is the major reason for enhancement of SPrC for the I_2 treatment. Liu et al. (2004) also reported that wheat seed protein content was enhanced under water deficiency conditions.

In both years, the maximum SPrC was found in the F_5 treatment, whereas the minimum SPrC was obtained in F_2 and F_1 in 2008 and 2009, respectively (Table 6). These results showed that mixing natural zeolite, especially in the highest amount (21%), with manure carries a negative charge balanced by freely moving cations with positive charges. This provides an ideal trap for cations such as NH_4^+, which are then released when required by plants. Natural zeolite has a very open framework with a network of pores that provide a large surface area for trapping and exchanging valuable nutrients. In the integrated treatment with 21% zeolite (F_5), greater N availability appears to have caused an increase in SPrC.

3.7. Seed P content (SPC) and seed K content (SKC)

Seed P concentration increased by 6% in 2009 compared to 2008 (data not shown). This may be due to the higher amounts of P in the soil and in the applied manure in 2009 compared to 2008 (Tables 1 and 2). Mean comparisons of fertilizer treatments showed that SPC was significantly higher in F_2–F_5 treatments than for F_1 (Table 6). There is evidence in the literature to suggest that the application of organic materials (such as composted manure) to soil may increase P solubility (Herenica et al., 2007; Edmeades, 2003). There are various possible mechanisms by which P availability and absorption can be enhanced by application of organic matter: (i) the use of organic amendments with a higher P content can increase P concentration in soil; (ii) the decomposition of organic matter in soil can increase the concentration of organic acids that reduce P sorption to the soil and thus increase P availability (Laboski and Lamb, 2003); and (iii) an increase in microbial biomass in organic or integrated plots can increase P availability. Microbial biomass increases when organic matter is added to the soil, increasing the release of CO_2, which in turn forms H_2CO_3 in the soil solution. The resulting weak acid can dissolve primary phosphorus-containing minerals, thereby increasing P availability.

In both years, water deficiency conditions reduced SKC. This effect was more pronounced in 2008 than 2009 (SKC in the I_1 treatment was 17 and 9% lower than the I_2 treatment in 2008 than 2009, respectively) (Table 8). Among the three major mechanisms affecting plant absorption of elements, diffusion is the most influential for K (Schaff and Skogley, 1982). As soil water potential is reduced, the diffusion coefficient decreases, thus reducing K absorption and consequently decreasing in SKC under water deficiency.

Seed K concentration was higher in F_5 (in 2008) and F_4 and F_5 (in 2009) than in other fertilizer treatments (Table 6). Manure directly contributes to the concentration of soil K and its uptake by plants, and zeolite also has a positive effect on K absorption. The type of zeolite applied in this study contains a high amount of K, and it has been reported that these types of zeolites directly increase K availability in soil (Rehakova et al., 2004). Therefore, it appears that SKC enhancement in the F_4 and F_5 treatments is related to the high availability of this element due to the application of manure and zeolite.

3.8. Irrigation water productivity (IWP) and soil cation exchange capacity (CEC)

Irrigation water productivity describes the quantitative relation between plant growth and water consumption. It is defined as dry matter produced (kg) per unit of water consumption (m^3) (Sezen et al., 2011). Table 8 shows that in both years, the I_2 treatment had greater IWP than the I_1 treatment. In other words, water use efficiency increased during limited water conditions. For the I_1 treatment, IWP was lower due to increased water deep percolation and evaporation. Maximum and minimum values of IWP were observed in F_5 in 2009 (0.73 kg m^{-3}) and F_1 in 2008 (0.50 kg m^{-3}), respectively (Table 7). In integrated treatments with zeolite (F_3, F_4 and F_5), application of manure increased soil water retention capacity (data not shown). This effect is due to hydrophilic components of manure, such as polysaccharides (Lima et al., 2009). Furthermore, zeolite improved growth and development of plants and increased dry matter production by prolonging N availability. Thus, the higher IWP in integrated treatments with zeolite can be explained by two separate processes: increased water retention due to manure application and better plant growth and development due to the presence of zeolite.

Table 9
Mean comparison of interaction effect of Irrigation regimes × fertilizer treatments.

Irrigation regimes × fertilizer treatments effect sliced by irrigation regimes for N.L			Irrigation regimes × fertilizer treatments effect sliced by irrigation regimes for P.L		
Irrigation regimes	Fertilizer treatments	N.L (kg ha^{-1})	Irrigation regimes	Fertilizer treatments	P.L (kg ha^{-1})
Full Irrigation	F1	36 a	Full Irrigation	F1	1 c
	F2	31 b		F2	15 a
	F3	28 bc		F3	13 a
	F4	25 cd		F4	10 b
	F5	22 d		F5	11 b
Limited Irrigation	F1	15 a	Limited Irrigation	F1	1 b
	F2	13 a		F2	6 a
	F3	14 a		F3	6 a
	F4	11 a		F4	5 a
	F5	10 a		F5	5 a

N.L, nitrate leaching; P.L, P leaching.
Means within each column of each section followed by the same letter are not significantly different ($p \leq 0.05$).
F1, urea; F2, urea + composted manure (CM) with 0% (w/w) zeolite; F3, urea + CM with 7% (w/w) zeolite; F4, urea + CM with 14% (w/w) zeolite; F5, urea + CM with 21% (w/w) zeolite.

Soil cation exchange capacity (CEC) is an important soil property that affects plant nutrient availability. Table 7 shows that manure and zeolite application tend to increase CEC in both years. Lima et al. (2009) reported that manure application to soil can increase CEC by releasing compounds such as lignin that absorb cations. In addition, zeolite increases CEC because the cation exchange capacity of zeolite is inherently high.

3.9. Nitrate leaching (NL) and P leaching (PL)

Nitrate leaching was more than 50% higher in 2008 than 2009 (Table 5) because nitrate concentrations and water percolation were 25 and 28% higher, respectively, in 2008 than in 2009. Among all treatments, maximum and minimum NL were obtained with I_1F_1 (36 kg ha^{-1}) and I_2F_5 (11 kg ha^{-1}), respectively. Averaged for both years, chemical treatments (F_1) had the highest NL (Table 9). This was expected, given the sandy soil and absence of soil amendments (compost or zeolite). In contrast, the integrated treatments (F_2–F_5) significantly decreased NL as compared to the F_1 particularly under full irrigation (Table 9). The effect of manure application on NL has been evaluated by several researchers, but the results of those studies are contradictory. Evanylo et al. (2008) and Leclerc et al. (1995) demonstrated that composted manure reduced NL. Other reported that manure application can increase NL (Basso and Ritchie, 2005; Yan-wang et al., 2002). It seems that the application of composted manure in these experiments decreased NL because manure improved the physicochemical conditions of the soil and increased the activity and penetration of plant roots.

The results showed that mixing 21% zeolite with manure was most effective for reducing NL from the rooting zone. With full irrigation, NL was reduced by 27 and 36% by F_5 when compared to F_2 and F_1, respectively (Table 9). The F_5 treatment also decreased NL in the limited irrigation regime, but its impact was more pronounced in the full irrigation regime (Table 9). The most important process by which zeolite application decreases NL arises from the unique properties of this natural mineral. In zeolites such as clinoptilolite, the pores are so large that cations such as ammonium can fit therein, but bacteria, particularly nitrifying bacteria, cannot access the zeolite pores (Baerlocher et al., 2001). Therefore, when ammonium is available in manure or soil, clinoptilolite selectively absorbs ammonium (Mumpton, 1999) and renders it unavailable to nitrifying bacteria, which are active in well-aerated sandy soils. Thus, the transformation of ammonium to nitrate (the latter of which is prone to leaching) will decrease with zeolite addition, thus decreasing NL.

Among fertilizer treatments, F_1 under both irrigation regimes had the lowest PL (Table 9). Among integrated treatments under full irrigation, F_2 and F_3 treatments showed the highest PL, while F_4 and F_5 treatments showed the lowest PL (Table 9). Generally, integrated treatments generated more PL than did the chemical treatment. As explained by Sharpley et al. (1994) and Edmeades (2003), applying sufficient manure to meet all N demand, while desirable from the point of view of minimizing NL, leads to soils becoming excessively enriched with P. This arises because of the high ratio of P relative to N in manure, which does not match plant nutrient demand. Various methods for overcoming this problem have been suggested. Shepherd and Withers (1999) stated that manure should be used rotationally, for example, one in every three years. Another method is to adjust the N:P ratio in manure using either chemical fertilizers or other organic sources with different N:P ratios. Eghball and Gilley (1999) suggested that manure can be used only to meet the P needs of the crop, while the crop's N requirement can be supplied via chemical fertilizer. More research is needed on the P concentration of manure and on mechanisms of P leaching after manure application to soil. Although the application of zeolite to integrated treatments – especially under full irrigation conditions – decreased PL, results showed that zeolite is more efficient at reducing NL than reducing PL. This highlights the need for attention to nutrient leaching, especially P leaching, when using manure as a soil amendment.

4. Conclusions

This study compared the effects of full and limited irrigation regimes associated with different fertilizer treatments under semi-arid climatic conditions on various aspects of sunflower production. Limited water application (the I_2 treatment) led to optimum irrigation water productivity but also caused a decline in seed yield. The results herein clearly indicate that the application of fresh manure with 14–21% zeolite by weight was considerably more effective than the chemical treatment (F_1) or the integrated treatment without zeolite (F_2) for improving most quantitative and qualitative sunflower traits. For sunflower production in poor sandy soil, a combined application of zeolite, composted manure and chemical N is recommended to ensure an acceptable seed yield (of agronomic importance) and for soil and water protection from excess N leaching (of economical and environmental importance). Reduction of N leaching in the presence of natural zeolite, such as clinoptilolite, increases plant-available N and consequently increases N use efficiency. Higher N use efficiency can not only alleviate environmental pollution but also enhance crop yield. It was also found that application of soil amendments such as zeolite with composted manure improved soil properties such as soil CEC (cation exchange capacity). Our results revealed that soil amending with manure and zeolite can be a beneficial approach for decreasing chemical fertilizer application rates and improving the sustainability of agricultural systems. Overall we concluded that combined application of zeolite and manure in a sandy soil promoting an acceptable sunflower seed yield (agronomic importance) and prevents high nutrient leaching (economical and environmental importance).

Acknowledgement

This research was supported by the Iran National Science Foundation (INSF) project number: 86015/01.

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