

**THE EFFECTS OF CLINOPTILOLITE APPLICATION ON GROWTH AND NUTRIENT IONS CONTENT IN RICE GRAIN**

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**ABSTRACT**

The experiment was carried out at the experimental fields of the Field Crops Department, Faculty of Agriculture, Ege University during the growth period of 2003 and 2004. Split-plots experiment design with three replications were used. The main plots were clinoptilolite applications (with 6 t ha<sup>-1</sup> and without treatment) and the sub-plots were rice varieties. Average yield of the varieties was approximately 11 % higher in the first plots with clinoptilolite application than untreated plots (the second plots without clinoptilolite). It was observed that clinoptilolite affected yield components positively. It decreased sterility (9.3 %) on the other hand, increased protein content (9.7 %) and macro-micro mineral in grain.

**Key words:** Rice, Zeolite, Clinoptilolite, Yield Component, Quality

**INTRODUCTION**

Zeolite means, “boiling stone” and was discovered in 1756 by the mineralog Fredrich Cronstedt (Mumpton, 1978).

Today, there are more than 40 natural zeolite minerals and more than 150 synthetic zeolite species are known. Among 40 species exist in nature, clinoptilolite is usually used for agricultural activities. Mordenite, chabazite, erionite and analcime are the other common types.

The zeolite mineral has a large isomorphic place changing capability. Because of these properties, zeolite has a high cation changing capacity and the characteristics of being selective at the cation absorption from soil solution. It has been recorded that monovalent cations and especially NH<sub>4</sub> are kept more than divalent cations (Flanigen, 1981).

Zeolite has a large usage area. It is increasingly used as fertilizer (Lewis et al., 1984) to remove the heavy metal content of industrial waste water and the soil (Mineyew, 1990) and as a soil order keeper (Mac Kown, 1978). Zeolite is successfully used for growing many crops such as grain, vegetables, grape and fruits (Burriesci et al., 1984). Clinoptilolite increases the effect of the fertilizer used in agriculture, and it provides a good plant growth. Clinoptilolite was used by many researchers in different dosages, and they reported a positive effect on efficiency (Bakhnova et al., 1999 and Uher et al., 2004). At the same time, Weber et al., (1983) and Kavosia (2007) were reported that clinoptilolite increased the major and minor mineral up take from the soil.

The zeolite mixed into the fertilizer helps the soil to hold the nutrients. So, it increases the absorbing capacity of the soil, and in the long term, it improves the soil quality. Behaving like slowly dissolving fertilizers, it improves the water balance and the absorbing capacity, especially, the light sandy soils. Therefore, it provide higher yields and better quality. Zeolite helps to have a favorable condition for nitrification by arranging the physical properties of the soil (Ünver et al., 1984).

Zeolites can also hold water up to 60 % of their weight because they have a multipored structure and they are in a mineral group of cage-like structure, which appears naturally.

The objective of this study was to investigate the effects of clinoptilolite on rice yield and some agronomic characters and nutrient content of rice grain.

### MATERIALS AND METHODS

This research was carried out during the rice growing period of 2003 and 2004 (Menemen, Izmir, Türkiye). Meteorological data of experimental sites were given in Table 1 (Anonymous, 2004 and 2005).

The soils of the experiment field were sandy-loamy with a little alkali reaction, rich in lime and useful potas content, have only little organic material, moderate values of total N and useful P and a low ratio of meltable total salt.

Irrigation water, was obtained from underground was third class of saltiness, first class of alkaliness and it showed a class of C<sub>3</sub>S<sub>1</sub> irrigation water. There was not any problem with respect to boron element in terms of the irrigation water. The experiments were conducted in the split-plot design with three replications. The main plot was applications (with and without clinoptilolide) and the sub-plots were warieties. The main plots was 54 m<sup>2</sup> and the sub-plots were 18 m<sup>2</sup>. Total experimental area was 324 m<sup>2</sup> (18 m<sup>2</sup> x 3 (varieties) x 2 (application) x 3 (replicates)).

Table 1. Main climatic characteristics of the experiment fields in Menemen.

<b>2003</b>	May	June	July	August	September	October
Average temperature (°C)	21.3	27.2	28.6	28.5	22.5	19.7
Rainy days	5.0	1.0	0.0	0.0	0.0	8.0
Total rainfall (mm)	8.5	0.8	0.0	0.0	0.0	68.5
Relative humidity (%)	52.5	37.5	37.0	38.2	46.9	51.8
Average sunshine (hours)	9.0	11.8	12.3	11.1	9.2	6.8
<b>2004</b>	May	June	July	August	September	October
Average temperature (°C)	20.3	26.5	29.0	27.8	23.8	19.8
Rainy days	5.0	2.0	1.0	0.0	0.0	3.0
Total rainfall (mm)	10.7	1.6	1.8	0.0	0.0	1.6
Relative humidity (%)	48.4	45.1	37.3	45.6	49.0	54.2
Average sunshine (hours)	8.8	10.4	12.0	10.3	9.1	7.5

The application dosage of clinoptilolite was 6000 kg ha<sup>-1</sup>. 600 g m<sup>-2</sup> clinoptilolite was given by hand and then was mixed to the soil surface with rake. The chemical

content of the analysis of the clinoptilolite clay mineral are shown in Table 2. The rice varieties used in the experiment were Baldo, Toag92 and Karacadağ.

The water depth was 40 cm in the field at the maximum growing stage. The planting time was on 21 June in 2003 and on 28 June 2004, respectively. Rice planting was carried out as second crop after harvesting the winter crop.

Mineral nitrogen was applied in three portions as  $\text{NH}_4^+$  with  $60 \text{ kg ha}^{-1}$  the rate of one part of nitrogen at sowing, second part at tillering and third part at panicle formation stage (Kacar, 1986). The phosphorus,  $80 \text{ kg ha}^{-1} \text{ P}_2\text{O}_5$  and Potassium  $40 \text{ kg ha}^{-1} \text{ K}_2\text{O}$  was used as basal fertilizer (Özbek, 1975).

Table 2. The chemical content and physical properties of clinoptilolite.

Chemical content							
	%		%	Ppm			
$\text{SiO}_2$	70.90	$\text{P}_2\text{O}_5$	0.02	Mn	38.0	Ph	6.63
$\text{Al}_2\text{O}_3$	12.40			Cu	2.90	Salinity %	0.03
$\text{Fe}_2\text{O}_3$	1.21			Zn	24.20	Lime %	1.06
$\text{K}_2\text{O}$	4.46			Sr	233.00	Water T.K.	46.60
MgO	0.83			Mo	<1.00	CEC(meq 100 g <sup>-1</sup> dry weight)	193.50
$\text{Na}_2\text{O}$	0.28			Cr	6.00	Na	36.40
CaO	2.54			Zr	22.50	K	61.00
$\text{TiO}_2$	0.089			Ba	65.00	Mg	22.10
MnO	<0.01			B	<10.00	Ca	74.00
Physical properties							
Bulk density					1000-1200 kg m <sup>-3</sup>		
Unit volume weight					2150- 2250 kg m <sup>-3</sup>		
Visible porosity (%)					39.40-44.20		

The weed cleared by hand and also the herbicide, propanil was applied. 20 days before the harvest, irrigation was stopped. And then, the plants were cut with sickle per harvesting and they left to dry in the field for a few days. After then, threshing was conducted. The moisture content of the grains was 11 % during weighting.

The data were recorded per the following characters rice yield, the number of tillers per plant, the number of grains per plant, 1000-grain weight (gr), plant length (cm), panicle length (cm), spikelet sterility, flowering time (days), protein content (%), head rice yield (%), husk rate and bran rate. The rice yield, yield components and other characteristics were determined according to the method of Standard Evaluation System for Rice (IRRI, 1988).

Dry matter content was determined on the flag leaves of the rice varieties approximately seven days before flowering stages. Macro and micro mineral contents on flag leaves was measured by Kacar (1972).

The data were analyzed by using SAS programme and the differences were ranged using the LSD test according to the 5 % probability.

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## RESULTS AND DISCUSSION

### **The Effect of Clinoptilolite on Some Agronomic Traits of Rice**

There were significant differences on rice yield between applications and varieties. The highest rice yield ( $3890 \text{ kg ha}^{-1}$ ) was obtained with the clinoptilolite treated plots (Table 3). Karacadağ rice variety had the highest grain yield ( $4700 \text{ kg ha}^{-1}$ ). The interaction between application x variety is shown in Table 3. According to the Table 3, at the first plots with clinoptilolite treatment, the average yield efficiency of the varieties ( $3890 \text{ kg ha}^{-1}$ ) was higher than at the un-uplicated second plots ( $3470 \text{ kg ha}^{-1}$ ); rice yield of the uplicated plots was 11 % higher than that of the un-uplicated second plots. The increase of grain yield was expected because of the physical and chemical properties of the zeolite. The cations ( $\text{NH}_4^+$ ) taken by clinoptilolite were given slowly back to the soil because of its high cation changing capacity ( $193.5 \text{ meq } 100 \text{ g}^{-1}$  dry weight) (Table 2). As a result of decreased nitrogen washing at rice puddles, nitrogen balance of the soil was improved. Therefore, it was concluded that the resulting enhanced availability of nitrogen, which affects the efficiency positively, may have caused the higher nitrogen efficiency of the puddles with clinoptilolite.

There were clear differences for the number of tillers per plant between applications and among varieties. The highest value was obtained with Karacadağ variety (4.8 number of tiller per plant) (Table 3). The Application x variety interaction was found to be statistically significant (Table 3). Chandler (1986) stated that the tillering of the rice plant was strongly affected by genetic factors and the amount of nitrogen in soil. Therefore it is expected that the plants on the plots, which are treated with clinoptilolite, has more productive tillers due to clinoptilolite physical and chemical properties.

Statistically significant differences were observed between applications and among varieties with respect to the number of grains per plant. Nevertheless, the application x variety interaction was not significant (Table 3). The carbohydrate accumulation in the piece is materialized through photosynthesis during piece binding (Yoshida, 1972). On the other hand, it was determined that the plant couldn't use nitrogen efficiently at low solar radiation (Evans and de Datta, 1979). Wada (1973) expressed that the number of fertile grains decreased at shadow and at lower solar radiation. Higher solar radiation and sunshine, on the other hand, increases the number of pieces at bunch. When the meteorological data of the trial years (2003 and 2004), was examined; it showed that there was not an important difference between years regarding the values of average temperature and sunshine duration along the months of June, July and August when the vegetative growth have took place (Table 1).

The number of fertile grains per plant was higher for the varieties, treated with clinoptilolite. The reason for this influence is thought of to be the mineral structure, and physical and chemical properties of clinoptilolite of which cation-changing capacity is high ( $193.5 \text{ meq } 100 \text{ g}^{-1}$  dry weight) (Table 1). Indeed, the positive effect of these properties on the number of grains per plant was also appeared on the number of tillers (Table 3).

Significant differences were observed for 1000-grain weight among varieties and between applications. The highest 1000-grain weight was obtained from Baldo variety (37.8 g). On the other hand, 1000-grain weight was found higher at clinoptilolite applications (32.7 g). The interaction between application x variety was not significant (Table 3). Gevrek, (1995) found that the effect nitrogen applications was not statistically significant on 1000-grain weight. Maurya et al. (1987) and Patra (1989), however,

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detected a statistically significant increase in 1000-grain weight with increased levels of nitrogen.

The characteristics such as plant height, panicle length and spikelet sterility are morphologic traits of the rice. The differences for all these traits are found to be statistically significant at 0.05 for both the applications and varieties. It is seen in Table 3 that, clinoptilolite was resultation to shortened panicle length (16.5 cm), increased plant height (85.2 cm) and decreased spikelet sterility (9.3 %). There is significant interactions for these characters between application x variety (Tablo 3). Plant height is an important character in rice especially, because of its effect on lodging. The high nitrogen levels cause lodging. Consequently, productivity and quality are negatively affected. Therefore, it is necessary to be careful while applying nitrogen at the areas where clinoptilolite is applied and where the tall rice varieties are grown.

Because the panicle length of rice has a low degree of heritability (25-50 %), this characteristic is affected more by the environmental factors. When the plant gets higher competition for sun, water and nutrient needs, occur so, the high plants appear with short bunches. At the main plot where clinoptilolit is used, the variety of high plants could have caused short bunches. Low and high heats forge some defects in rice in the vegetative and generative phases, resulting in a big loss of productivity (Gevrek, 1995). Pollens die and the sterility (empty ears) begins at booting stage when high temperature 35 °C and low temperature 20 °C appears (Wada, et al., 1973). It is a good chance that the sterility rate of the plots where clinoptilolite was applied was less than that in the plots without cilinoptilolite.

The difference for flowering time among the rice varieties was found to be significant. Based on the LSD test results, Toag92 had the shortest flowering time (53.5 days). On the other hand, there was not a statistically significant difference between the flowering times for the applications. Also the application x variety interaction was not significant (Table 3).

No statistical analysis were carried out regarding the protein content (%), as, in both of the trial years, the relevant analysis was performed with no replications. However, in Table 3, it is seen that clinoptilolite has a positive effect on protein contents of rice varieties. The biggest fraction of rice protein is glutelin and it has the nitrogen rate of 16.8 %. Hence, it may be concluded that, the high protein conteint (%) of the rice plants grown on the plots with clinoptilolite can be caused by their ability to raise more nitrogen from soil due to clinoptilolite.

Weber et al., (1983) reported that 13.5 t da<sup>-1</sup> clinoptilolite decreased the NH<sub>4</sub>-N loss from the soil. Kavosia (2007) reported that clinoptilolite accumulated the nitrogen in the soil and it made easier to uptake the nitrogen by the plant. This caused higher protein rate in grain (Table 3).

Table 3. The effect of clinoptilolite application on some agronomical and quality traits of rice varieties grown in Menemen, Izmir, as the approximately of 2003 and 2004.

	Rice yield (kg ha <sup>-1</sup> )	Number of tiller plant <sup>-1</sup>	Num. of grain plant <sup>-1</sup>	1000 grain weight (g)	Plant height (cm)	Panicle length (cm)	Flowering time (days)	Spikelet sterility (%)	Pprotein Content (%) <sup>a</sup>	Head rice yield (%)	Husk rate	Bran rate
I. Apl.	3890.0 a	4.1 a	250.0 a	32.7 a	85.2 a	16.5 b	70.1	9.3 b	9.7	62.1 a	21.2	7.4 b
II. Apl.	3470.0 b	3.1 b	220.0 b	31.7 b	81.4 b	17.1 a	70.8	10.1 a	8.9	60.9 b	21.2	8.1 a
LSD (005)	<b>82.27</b>	<b>0.126</b>	<b>23.519</b>	<b>0.125</b>	<b>0.906</b>	<b>0.193</b>	<b>ns</b>	<b>0.134</b>		<b>0.532</b>	ns	<b>0.596</b>
Baldo	3060.0 c	2.6 c	179.2 b	37.8 a	82.1 b	15.9 b	73.6 b	11.9 a	10.0	60.9 b	20.7 b	8.1
Toag92	3290.0 b	3.4 b	183.0 b	33.1 b	63.6 c	15.5 c	54.0 c	9.5 b	10.3	61.2 ab	21.4 a	7.8
Karacada	4700.0 a	4.8 a	343.0 a	25.5 c	104.3a	18.9 a	83.9 a	7.8 b	7.6	61.7 a	21.5 a	7.3
LSD(005)	<b>101.32</b>	<b>0.155</b>	<b>28.805</b>	<b>0.153</b>	<b>1.109</b>	<b>0.235</b>	<b>3.064</b>	<b>0.164</b>		<b>0.652</b>	<b>0.656</b>	<b>ns</b>
Baldo	3160.0 c	3.1 c	200.0	38.0	86.0 b	15.5 b	73.5	10.6 a	10.3	61.3 b	21.1	7.8
Toag92	3460.0 b	5.8 a	196.0	34.0	65.0 c	15.0 c	53.5	9.6 b	11.1	62.6 a	21.5	8.2
Karacada	5080.0 a	5.4 b	368.0	26.1	104.8 a	19.0 a	83.5	7.7 c	7.8	62.4 a	21.1	6.4
Baldo	2950.0 c	2.2 c	158.0	37.6	78.2 b	16.4 b	73.6	13.2 a	8.8	60.5 ab	20.3	8.9
Toag92	3110.0 b	3.0 b	170.0	32.2	62.0 c	16.0 c	54.4	9.4 b	9.4	59.8 b	21.5	7.2
Karacada	4350.0 a	4.1 a	306.0	25.0	103.8 a	18.9 a	84.3	7.8 c	7.4	61.0 a	21.8	8.0
LSD(005)	<b>143.280</b>	<b>0.219</b>	<b>ns</b>	<b>ns</b>	<b>1.569</b>	<b>0.334</b>	<b>ns</b>	<b>0.637</b>		<b>0.922</b>	<b>ns</b>	<b>ns</b>
Application	112.0**	258.3**	90.8**	286.0**	50.7**	549.9**	ns	33.6**		40.7**	ns	6.1*
F values	661.1**	395.5**	6.7**	14215.0*	2745.8**	40.0**	211.5**	4.9**		4.4*	4.3*	ns
AplxCult.	13.0**	7.1**	ns	ns	29.1**	13.0**	ns	49.5**		6.8*	ns	ns

\*\* , \* , and ns: represent the significance levels of 0.01, 0.05, and no significance, respectively.

<sup>a</sup>: Because of the protein content have two replications the data were not statistically analyzed.

I. Apl: the first plots with clinoptilolite application.

II. Apl: the second plots without clinoptilolite application

When the effect of clinoptilolite to the head rice yield is examined, it was seen that the difference of this characteristic is statistically significant and clinoptilolite increases the head rice yield (from 60.9 to 62.1) (Table 3).

According to the results of the variance analysis, there is an obvious interaction between application x variety (0.05). A head rice yield is very important for a good price. It is desirable to get the total milled rice (more than 70 %) and head rice yield (more than 50 %) (Khush et al., 1978). The head rice yield changes according to varieties, years, ecological conditions, used technology and growing techniques (Wada et al., 1973). The head rice yield pretty much variety related characteristic but it was underlined by many researchers that the head rice yield (%) was also affected by nitrogen application as well (Gevrek, 1995). Indeed, because of clinoptilolite's property to take the  $\text{NH}_4^+$  from soil and then to give it slowly back to the area, spreading it to all growing period, the head rice yield (%) is more in the first plots with clinoptilolite application than in the second plots (without clinoptilolite).

The husk rate was not significantly different for applications. It is significant for varieties. Neither statistically significant application x variety interaction was found with respect to the husk rates (Table 3).

Besides, concerning the bran rate, only the difference between the applications is found to be statistically significant, and there was not a significant difference between applications (Table 3).

## 2. The Effect of Clinoptilolite on Macro and Micro Mineral Contents of Rice Plant

The results of macro and micro mineral analysis on the flag leaves of the rice varieties are given in Table 4 and 5 for the year 2003. It is seen that the macro and micro mineral values are higher at clinoptilolite application than the without application.

To determine the effect of clinoptilolite on macro and micro mineral accumulation on the head rice, the results of the macro and micro mineral analysis of head rice from paddy with and without Clinoptilolite are compared in Tables 6 and 7. It is seen that, like in the flag leaves, clinoptilolite has an additional effect on the macro and micro mineral accumulation. Our findings were supported with the results of Weber et al. (1983) and Kavosia (2007).

Table 4. Clinoptilolite's effect of macro mineral accumulation of flag leaf in rice (2003).

	Macro minerals												
	N (%)		P (ppm)		K (ppm)		Ca (ppm)		Mg (ppm)		Na (ppm)		
	+	-	+	-	+	-	+	-	+	-	+	-	
Baldo	0.7	0.6	378.0	231.0	10400.	0	9400	5200.0	4000.	3060.	2938.	7000	4000
Toag9	1.1	1.0	441.0	357.0	9800.0	7000	6000.0	5200.	1244.	1224.	6000	5000	
2								0	0	0	.0	.0	
K.Dağ	0.9	0.8	336.0	294.0	10600.	9800	7200.0	6000.	1489.	1387.	6000	4000	
					0	0	0	0	0	0	.0	.0	
Aprox.	0.9	0.8	385.0	294.0	10267.	8733	6133.0	5067.	1931.	1850.	6330	4300	
					0	0	0	0	0	0	.0	.0	

+: containing clinoptilolite, -: non containing treatment

Table 5. Clinoptilolite's effect of micro mineral accumulation of flag leave in rice (2003).

	Micro minerals							
	Fe (ppm)		Cu (ppm)		Zn (ppm)		Mn (ppm)	
	+	-	+	-	+	-	+	-
Baldo	369.0	273.0	4.4	3.3	30.2	22.3	440.7	432.4
Toag92	250.0	220.0	4.4	4.4	30.0	19.7	395.6	366.1
K. Dağ	333.0	271.0	4.4	4.3	33.4	26.7	462.8	423.2
Aprox.	317.0	255.0	4.4	4.0	31.2	22.9	433.0	407.3

+: containing clinoptilolite, -:non containing treatment

Table 6. Clinoptilolite's effect on macro mineral accumulation of milled rice (2003).

	Macro minerals											
	N (%)		P (ppm)		K (ppm)		Ca (ppm)		Mg (ppm)		Na (ppm)	
	+	-	+	-	+	-	+	-	+	-	+	-
Baldo	1.7	1.7	462.0	388.5	600.0	400.0	50	trace	trace	trace	25.0	25.0
Toag92	1.8	1.6	504.0	231.0	600.0	300.0	35	trace	trace	trace	50.0	25.0
K. Dağ	1.3	1.3	367.5	294.0	400.0	500.0	trace	trace	trace	trace	50.0	25.0
Aprox.	1.6	1.5	444.5	304.5	533.0	400.0	trace	trace	trace	trace	42.0	25.0

+: containing clinoptilolite, -:non containing treatment

Table 7. Clinoptilolite's effect on micro mineral accumulation of milled rice (2003).

	Micro minerals							
	Fe (ppm)		Cu (ppm)		Zn (ppm)		Mn (ppm)	
	+	-	+	-	+	-	+	-
Baldo	12.0	9.6	1.8	1.8	13.7	13.3	5.5	5.5
Toag92	12.0	9.6	2.4	1.8	13.2	13.0	7.4	5.8
K. Dağ	9.6	2.4	1.8	1.8	10.6	10.3	4.0	3.7
Aprox.	11.2	7.2	2.0	1.8	12.5	12.2	5.8	5.0

+: containing clinoptilolite, -:non containing treatment

## CONCLUSION

The clinoptilolite applied plots had 11 % higher rice yield than unapplied plots. It was observed that clinoptilolite affected positively yield components. It caused a decrease in spikelet sterility (9.3 %) an increase in protein content (9.7 %) and macro-mineral content of rice grain. However, in rice production, it will be more beneficial to keep on studies on the dosage of clinoptilolite in order to make the best use of it.



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