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Reduction of Nitrate Nitrogen from Alkaline Soils Cultivated with Maize Crop Using Zeolite-Bentonite Soil Amendments

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Abstract

The present study examines the efficiency of soil amendments regarding the retention of nitrate ions, from maize (*ZEA MAYS*). The experiments were performed in May – June 2010 at the greenhouse of the University of Thessaly in Volos (Central Greece). The soil amendments that have been used for the experiments were zeolite, bentonite and zeolite – bentonite in a proportion of 3:1 w/w. Two doses of nitrogen were used (400 and 800 kg N ha^{-1}) in the form of NH_4NO_3. Nine treatments occurred; six of them contained soil amendments. Each treatment repeated three times. According to the statistical analysis of the greenhouse experiments' data, bentonite and zeolite – bentonite increased the height of the plants in the dose of 800 kg N ha^{-1}. Moreover, all the used soil amendments reduced the concentration of nitrate nitrogen in soil and plants. Consequently, such materials can be used for the remediation of polluted soils with nitrogen and the production of high quality products.

Keywords: Bentonite; Zeolite; Nitrate nitrogen; Maize

Introduction

Most of the nitrogen (97–98%) in the soil is found in the organic matter and unavailable to plants. The percentage of nitrogen in the inorganic form such as nitrate (NO_3^-) and ammonium (NH_4^+) ions, which are available to plants, is only 2–3%. During the appropriate conditions of moisture, temperature and oxygen content, microorganisms are breaking down the organic matter, which is released as inorganic nitrogen into the soil (mineralization). During the mineralization process, most of the organic matter is first converted to ammonium (NH_4^+) and then to nitrate (NO_3^-) through the nitrification process, leading to the availability of nitrate ions by crops and microorganisms. Nitrates are very mobile in the soil. Most plants absorb the majority of their nitrogen in the nitrate (NO_3^-) form and in the ammonium (NH_4^+) form to a lesser extent [1,2].

Maize crops respond strongly to nitrogen (N) supply. Fertilizers enriched with nitrogen lead to high crop yields but such process also increases the risk of nitrate leaching and groundwater contamination. To achieve financial profitability and environmental sustainability, except for resource management rules, the use of soil amendments is the necessary measure to diminish the excess quantity of nitrogen from soil and crops [3].

Zeolite and bentonite are naturally occurring structured and silicate minerals, respectively, with high cation exchange and ion adsorption capacity. Zeolites are hydrated aluminosilicates of alkaline and alkaline-earth minerals [4]. Their structure is made up of a framework of AlO_4^{5-} and SiO_4^{4-} tetrahedra linked to each other by sharing oxygen atoms. The substitution of Si^{4+} by Al^{3+} in tetrahedral sites results in more negative charges and a high cation exchange capacity [5]. Bentonite is a 2:1 mineral with one aluminum octahedral sheet and two silica tetrahedral sheets, which form a layer. Layers are held together by Van der Waals forces. Because of these weak forces and some charge deficiencies in the structure, water can easily penetrate between layers and cations balance the deficiencies [6].

The objective of this study was to evaluate the removal of nitrate nitrogen ions from soils cultivated with maize crop using soil amendments such as zeolite, bentonite and zeolite-bentonite.

Materials and Methods

Greenhouse experiments were conducted for the determination of zeolite (Z), bentonite (B) and zeolite – bentonite (Z-B) in a proportion of 3:1 Z/B w/w. as soil amendments. Zeolite and bentonite was bought from S&B Company (Greece). Specifically, 1 kg of soil, 1.0 g of each soil amendment and 100 mg N kg^{-1} (400 kg N ha^{-1}) or 200 mg N kg^{-1} (800 kg N ha^{-1}) in the form of NH_4NO_3 were added to plant pots. Then, plant seeds of maize were cultivated.

Four treatments were realized for each dose of nitrogen (4x2) but only three of them contained soil amendment (Table 1). Each treatment was repeated three times. As a consequence twenty seven treatments were realized (eighteen with soil amendments, six with no soil amendment but with nitrogen and three with no soil amendment and nitrogen). Forty five days after germination the plants were collected, their morphological characteristics were identified, NO_3^--N were determined in plant and soil by copperized cadmium method [7]. The experiments took place from May to June 2010. The physicochemical characteristics of soil, which was selected from Velestino area in Volos (Central Greece), show soil pH equal to 8.82, low concentrations of organic matter (<2.3%) and nitrogen (<0.22%). The water storage capacity of soil remained stable at 65% and the temperature ranged from 25-35°C. The statistical results of the greenhouse experiments were analyzed by LSD test with significance 95% ($p<0.05$) using Strat graphics Plus 8.1.

The titration method was used for the determination of the Zero Point of Charge (z.p.c.) of Bentonite (B) and zeolite-bentonite (Z-B). This method is based on curves of surface charge versus pH at

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different ionic strength of the supporting electrolyte (KNO_3). The point of intersection of the above curves corresponds to the p.z.c. Specific Surface Area (SSA) of Z-B material was determined by the BET method, using N_2 as adsorbate in Sorptomatic 1900 Carlo Erba Surface area analyzer [8].

The experimental values of each parameter, e.g. crop height, nitrogen in soil or crop, from C or F treatment, which were measured, compared to the respective theoretical values, which come from mixtures law, follows [9]:

$$C_{theor.} = x_1 \cdot A_{exp.} + x_2 \cdot B_{exp.} \text{ or } F_{theor.} = x_1 \cdot D_{exp.} + x_2 \cdot E_{exp.} \qquad (1)$$

where $C_{theor.}$ or $F_{theor.}$ is the theoretical value of the treatment according to the applied nitrogen dose, i.e. 400 or 800 kg N ha^{-1}, $A_{exp.}$ or $D_{exp.}$ is the experimental value of A or D treatment which contains zeolite as soil amendment at different nitrogen doses, $B_{exp.}$ or $E_{exp.}$ is the experimental value of B or E treatment which contains bentonite as soil amendment at different nitrogen doses, x_n is the weight percentage of the n soil amendment of the specific treatment.

Results and Discussion

Figure 1a shows that the use of soil amendments, i.e zeolite (Z), bentonite (B), zeolite-bentonite (Z-B) of A, B and C treatments, respectively, led to no significant statistical increase in the height of maize in correlation with the unamended control (G) for nitrogen dose equal to 400 kg N ha^{-1}. Comparing the experimental height of maize using Z-B as soil amendment ($C_{exp.}$ treatment) with the theoretical height of maize ($C_{theor.}$ treatment) using the laws of mixtures, the results are similar. On the contrary, the use of bentonite (E treatment) and zeolite-bentonite (F treatment) increased significantly the height of maize compared to the unamended control (G) for nitrogen doses around 800 kg N ha^{-1} (Figure 1b). Moreover, a significant decrease in the height of crops presented to soils enriched with zeolite (D treatment) as soil amendment.

Figures 2a and 2b shows that the use of bentonite (B treatment) and zeolite (D treatment) as soil amendments led to a statistical increase in the dry weight of crops compared to un-amended control (G) for nitrogen doses equal to 400 and 800 kg N ha^{-1}, respectively. Comparing the treatment with nitrogen but without soil amendment (H,I) with all the others which had soil amendments no statistical significant difference in the dry weight of plants was presented. Comparing treatments G (without soil amendment and nitrogen) and H, I (without soil amendment but with nitrogen), it seems that no statistical difference was presented to both nitrogen doses (Figure 2).

Comparing the experimental dry weight of maize using Z-B as soil amendment ($C_{exp.}$ or $F_{exp.}$ treatment) with the theoretical dry weight of maize using the law of mixtures ($C_{theor.}$ or $F_{theor.}$ treatment), the results showed small differences for the two doses of nitrogen.

The Zero Point of Charge (z.p.c.) of bentonite and zeolite was equal to 8.0 and 6.8 respectively (*Table 2*), while the soil solution pH was equal to 8.82. Since pH is higher than the z.p.c. of bentonite, negative charges are predominant and nitrates repelled from the region near the root system to deeper soil. Moreover, bentonite and zeolite appear also high specific surface area equal to 45.7 and 30.7 $m^2 g^{-1}$. Z-B amendment appears intermediate values of z.p.c. and specific surface area.

Comparing treatments H and I with all the others, it seems a statistical decrease in nitrate nitrogen to soils with soil amendments (Figure 3). For nitrogen dose equal to 400 kg N ha^{-1}, soil presented low concentrations of nitrate nitrogen using bentonite (B treatment) as soil amendment compared to all the other soil amendments (Figure 3a). Soil with zeolite as amendment (A treatment) presented the highest concentration of nitrate nitrogen while soil with Z-B (C treatment) presented intermediate values of nitrate nitrogen. Higher doses than 400 kg N ha^{-1} increased the toxicity of soil to nitrate nitrogen and the use of Z-B as soil amendment (F treatment) presented a significant decrease of its amount to soil compared to the other soil amendments *(*Figure 3b*)*. The increased amount of nitrate nitrogen in soil, which contained bentonite (E treatment), was caused due to the repelled nitrate ions from the root system through soil water, as it is illustrated in Figure 3b. Similar behavior presented also with the use of zeolite as soil amendment (D treatment) due to its negative surface charge.

A small amount of nitrate nitrogen in soils with Z, B and Z-B as amendments may be absorbed by soil amendments due to their extended porosity and high specific surface area. Comparing the experimental values of nitrate nitrogen in soil using Z-B as soil amendment ($C_{exp.}$ or $F_{exp.}$ treatment) with the theoretical values of nitrate nitrogen in soil using the law of mixtures ($C_{theor.}$ or $F_{theor.}$ treatment), the results showed no significant differences between them for the two doses.

As far as the uptake of NO_3^--N ions from crops is concerned, it seems that all soil amendments reduced significantly their uptake from crops but especially the addition of bentonite (B and E treatments) (Figure 4). The addition of bentonite to soil led to crops with the same NO_3^--N content as the unamended control (G). Moreover, Z-B soil amendment (F treatment) can also reduce significantly the amount of nitrate nitrogen in maize to the level of the unamended control (G treatment) (Figure 4b) in high nitrogen dose equal to 800 kg N ha^{-1}.

According to Figures 4a and 4b the addition of soil amendment to soil polluted with 400 and 800 kg N ha^{-1}, reduced significantly the amount of nitrate nitrogen to maize following the order: Bentonite (B) > Zeolite (Z) > Zeolite-Bentonite (Z-B) and Bentonite (B) > Zeolite-Bentonite (Z-B) > Zeolite (Z), respectively.

The repelled nitrate nitrogen ions from the root system of maize to the deep soil as a result of the negative charge of bentonite led to the lowest uptake of nitrate nitrogen from crops. Comparing the experimental nitrate nitrogen in maize using Z-B as soil amendment ($C_{exp.}$ or $F_{exp.}$ treatment) with the theoretical nitrate nitrogen in maize using the law of mixtures ($C_{theor.}$ or $F_{theor.}$ treatment), the results showed significant differences between them especially for the dose of 800 kg

Treatment	Maize cultivation	Amendment			Nitrogen dose	
		Z	B	Z-B	I	II
A	x	x	-	-	x	-
B	x	-	x	-	x	-
C	x	-	-	x	x	-
D	x	x	-	-	-	x
E	x	-	x	-	-	x
F	x	-	-	x	-	x
G	x	-	-	-	-	-
H	x	-	-	-	x	-
I	x	-	-	-	-	x

Table 1: Schematic representation of greenhouse experiments.

Specific surface area (SSA)			Zero point of charge (z.p.c.)		
	$m^2 g^{-1}$				
Z[a]	B[b]	Z-B	Z[a]	B	Z-B
30.7	45.7	34.5	6.8	8.0	8.7

[a,b] The characteristics of Z and B were calculated elsewhere [8,10]

Table 2: Physical and chemical characteristics of different soil amendments.

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	400 kg N ha^{-1}			800 kg N ha^{-1}		
Soil amendment	Treatments	% NO_3^- - N reduction in soil	% NO_3^- - N reduction in maize crop	Treatments	% NO_3^- - N reduction in soil	% NO_3^- - N reduction in maize crop
Zeolite (Z)	A-H	39.44	87.32	D-I	36.88	33.88
Bentonite (B)	B-H	57.40	98.05	E-I	17.89	98.27
Zeolite-Bentonite (Z-B)	C-H	48.36	73.87	F-I	46.33	91.57

Table 3: Percentage of NO_3^- - N reduction in maize crop cultivation of each soil amendment compared to treatments H (treatment with maize cultivation and nitrogen dose I) and I (treatment with maize cultivation and nitrogen dose II)

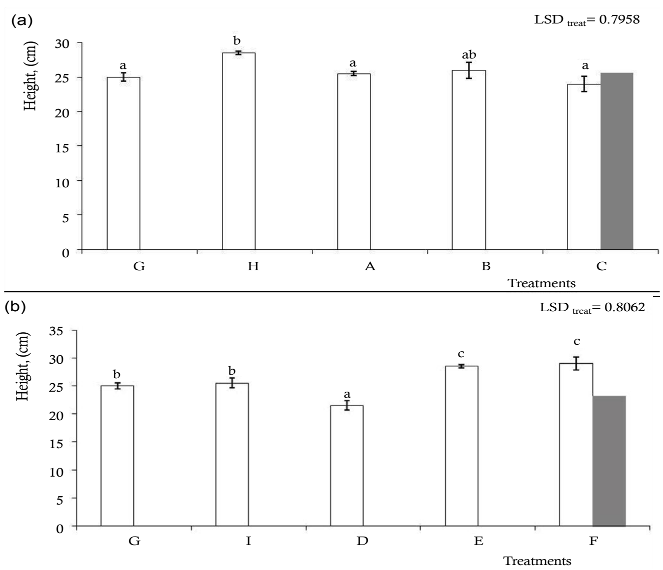

Figure 1: Impact of nitrogen and soil amendments on the height of maize for (a) 400 kg N ha^{-1} and (b) 800 kg N ha^{-1}, where treatments' symbols are explained in Table 1, C and F treatments present the experimental (C or F $_{exp.}$ – white color) and the theoretical (C or F $_{theor.}$ – grin color) values of each treatment, respectively.

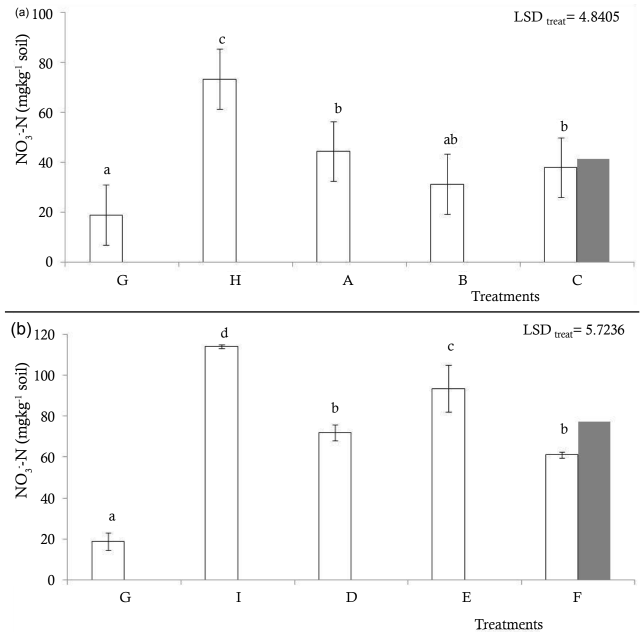

Figure 3: NO_3-N concentration in cultivated soil in correlation with soil amendments for (a) 400 kg N ha^{-1} and (b) 800 kg N ha^{-1}, where treatments' symbols are explained in Table 1, C and F treatments present the experimental (C or F$_{exp}$ –white color) and the theoretical (C or F$_{theor.}$–grin color) values of each treatment, respectively.

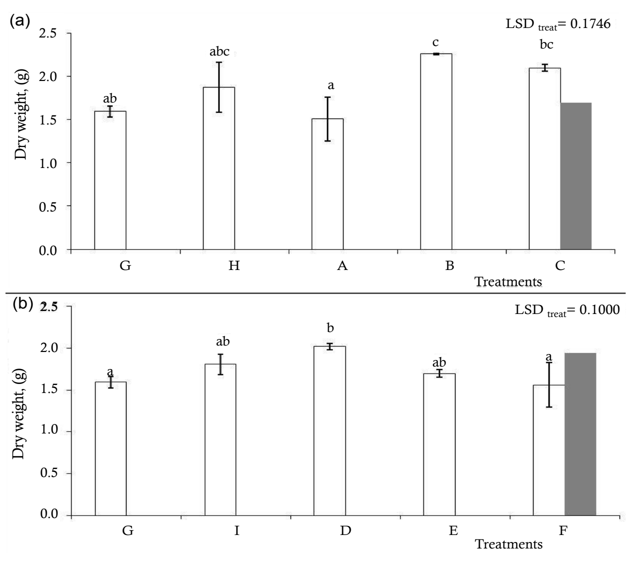

Figure 2: Impact of nitrogen and soil amendments on the dry weight of maize for (a) 400 kg N ha^{-1} and (b) 800 kg N ha^{-1}, where treatments' symbols are explained in Table 1, C and F treatments present the experimental (C or F $_{exp.}$ – white color) and the theoretical (C or F $_{theor.}$– grin color) values of each treatment, respectively.

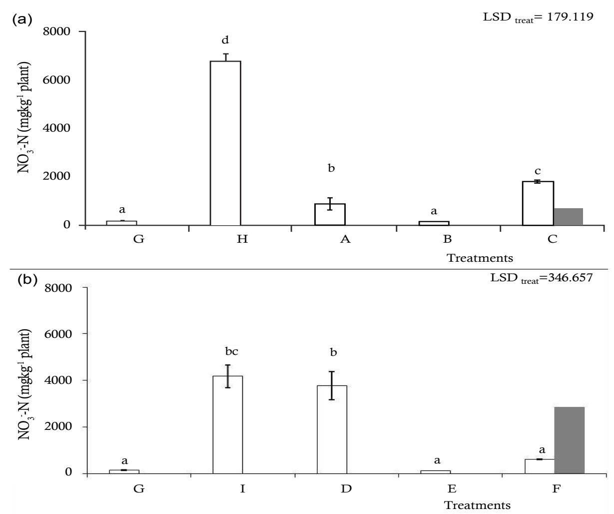

Figure 4: NO_3-N concentration in plants in correlation with soil amendments for (a) 400 kg N ha^{-1} and (b) 800 kg N ha^{-1}, where treatments' symbols are explained in Table 1, C and F treatments present the experimental (C or F $_{exp.}$ – white color) and the theoretical (C or F $_{theor.}$ – grin color) values of each treatment, respectively.

N ha^{-1} (Figure 4). Probably the high toxicity of the soil with nitrate nitrogen, led Z-B amendment ($F_{exp.}$ treatment) to have a similar behavior as bentonite (E treatment) although the amount of bentonite in Z-B is one third of the initial amount of bentonite.

The reduction percentage of NO_3^- - N in soil and maize crop cultivation appear in Table 3. From the above table, it seems that all materials presented high decrease of NO_3^- - N either to soil or maize crop, respectively. Zeolite and bentonite appeared the highest decrease of NO_3^- - N in maize crop for the addition of 400 kg N ha^{-1}. Moreover, bentonite and zeolite-bentonite presented the highest decrease of NO_3^- - N in maize crop for the addition of 800 kg N ha^{-1}. The comparison of treatments with soil amendment and different nitrogen doses (A,B,C,D,E,F) with the treatment G where only maize was cultivated is not acceptable due to the lack of additional nitrogen to treatment G.

Conclusions

- According to the results, soil amendments did not manage to increase the agronomic characteristics of maize, except for bentonite and Z-B, which managed to increase the height of the crop in the dose of 800 kg N ha^{-1}.
- No statistical significant difference in the dry weight of crops was presented with the use of soil amendments.
- All soil amendments decreased statistical significantly the nitrate nitrogen in soil and plant in both doses.
- Considering all soil amendments that were used, the most suitable for the removal of nitrate nitrogen from maize crop is bentonite and zeolite-bentonite for doses equal to 400 kg N ha^{-1} and 800 kg N ha^{-1}.
- The low concentration of nitrate nitrogen in maize crops cultivated in soil with bentonite as soil amendment was caused by the negative charges of bentonite which led to the repelled nitrate nitrogen ions from the root system of maize to the deep soil through soil water.

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