

CLINOPTILOLITE ZEOLITE INFLUENCE ON INORGANIC NITROGEN IN SILT LOAM AND SANDY AGRICULTURAL SOILS

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ABSTRACT

Development of best management practices can help improve inorganic nitrogen (N) availability to plants and reduce nitrate-nitrogen (NO₃-N) leaching in soils. This study was conducted to determine the influence of the zeolite mineral Clinoptilolite (CL) additions on NO₃-N and ammonium-nitrogen (NH₄-N) in two common Pacific Northwest soils. The effects of CL application rate (at least 12 tons/acre) either band applied or mixed with a set rate of nitrogen (N) fertilizer on masses of NO₃-N and NH₄-N in leachate and soil was investigated in a column study using a Portneuf silt loam (coarse-silty mixed mesic Durixerollic Calciorthid) and a Wolverine sand (Mixed, frigid Xeric Torripsamment). All treatments for each soil received a uniform application of N from urea fertilizer, with fertilizer banded or mixed with CL. In the Portneuf soil, band application of CL and N contained 109% more total inorganic N (NO₃-N + NH₄-N) in the soil/leachate system compared to mixing. In both soils, CL application rate influenced the quantity of NO₃-N and NH₄-N in the leachate and soil. Application of CL at rates of 3 to 6 tons/acre resulted in the conservation of inorganic N in the soils. Band applying CL and N appears to conserve available inorganic N in the soil compared to mixing CL and N possibly due to decreased rates of microbial immobilization, nitrification and denitrification.

INTRODUCTION

Nitrogen from fertilizers is needed to optimize and sustain crop production in agronomic systems, but is susceptible to leaching and denitrification loss from soils. Nitrogen losses due to leaching and denitrification from agricultural land, especially in sandy soils, are an environmental and economic concern (Perrin et al., 1998).

A means of lessening off-site N movement into waters, and in particular N from land applied N fertilizer, is by application timing and placing N fertilizers in bands below the soil surface. Incorporating urea in bands has been shown to reduce NH₃ emissions (Bouwmeester et al., 1985), reduce NO₃-N leaching (Williams et al, 2003), and reduce total N loss (Prasertsak et al., 2002). Fertilizer placement practices have been studied and introduced to directly or indirectly reduce N losses in many agricultural systems. However, other new technologies associated with soil conditioners, such as zeolite minerals, have the potential to further reduce soil N leaching losses.

Zeolites are naturally occurring aluminosilicate minerals (Kithome et al., 1998). They are composed of tectosilicates with isomorphous substitution of Al⁺³ and Si⁺⁴, and have high cation exchange capacities (CEC; Perrin et al., 1998). The theoretical CEC of the zeolite mineral Clinoptilolite (CL) is 220 cmolc/kg (Ming and Mumpton, 1989). Furthermore, the structure of CL makes the mineral highly selective for K⁺ and NH₄⁺, and less selective for Na⁺ and divalent cations such as Ca⁺² (Perrin et al., 1998). Theoretically, the affinity of CL for NH₄⁺ along with CL open mineral structure can potentially protect NH₄⁺ from microbial access and thus reduce nitrification rates.

A number of research projects have shown increased growth and/or yield of a variety of crops due to either an effect of zeolites on improved N use efficiency or reduced NH_4^+ toxicity (Huang and Petrovic, 1994). Research evaluating the effect of CL on $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ leaching through soil have also been reported. MacKown and Tucker (1985) found that mixing CL into a loamy sand at rates of 22, 47, or 93 tons/acre, with a constant rate of ammonium sulfate applied at 392 lbs $\text{NH}_4\text{-N}$ /acre, reduced $\text{NH}_4\text{-N}$ leaching through columns compared to a control. Nitrate-N was not measured due to the addition of a nitrification inhibitor with the N source. However, Huang and Petrovic (1994) found that mixing CL into simulated sand-based golf course greens at a rate equal to 10% of the soil mass (184 tons/acre) reduced $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ leaching through lysimeters compared to a control.

The purpose of the current study was to determine $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ leaching potential through common agricultural soils in the Pacific Northwest U.S. amended with an agronomic rate of N fertilizer and various rates of CL obtained from a local source.

METHODS

This study was conducted using soil columns in a climate controlled growth chamber. Each column was constructed from poly-vinyl chloride with a diameter of 4.2 inches and a height of 12.2 inches. Portneuf silt loam and Wolverine sand soils were collected from a depth of 0 to 12 inches in fields from southern Idaho. This study was conducted separately for each soil. Clinoptilolite was obtained from the Zeocorp LLC owned mine located in Hines, OR. Treatments for the Portneuf soil consisted of four CL rates (0, 3, 6, and 9 tons/acre) and two application methods of CL and N fertilizer (mixed and band). Treatments for the Wolverine soil consisted of four CL rates (0, 3, 6, 9, and 12 tons/acre) and the two CL/N application methods (mixed in top half and band applied at 6 inches). For each soil type, all CL rate treatments received a nitrogen fertilizer application rate of 200 lbs N/acre as urea. The N application methods mirrored the CL application methods because it would be logical in the field to apply the N with the CL. The total amount of soil in each column was 6.6 lbs. Each treatment combination and the control were replicated four times in a complete randomized design.

Reverse osmosis water was applied to all columns weekly for eleven weeks for each soil type. The total water applied over the duration of the study for both soil types was 11.3 inches. Leachate was collected in 500 ml glass bottles from each column during each water application date for each soil type. The volume of leachate was determined during each leaching event, and a subsample from each column was filtered (45 μm filter) and analyzed for $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ using a flow injection analyzer. Masses of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ were calculated by multiplying the concentrations by the volumes of leachate collected. The masses were reported on an area basis. The total $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ mass data (summed over all leaching events) are presented in this paper for both soils. Including data by leaching event did not add significantly to the conclusions inferred from the data.

Following the leaching portion of the study, soils were collected from each column in 2 inch increments from 0 to 10 inches. Soils were air-dried, sieved through a 5-mm screen, and analyzed for $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$. Masses of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ for each depth were calculated by multiplying the concentrations by the soil masses. The masses were reported on an area basis. As with the leachate data, the total $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ mass data (summed over all soil depths) are presented in this paper for both soils because data by depth did not significantly add to the

inferred conclusions. Combined data from the soil and leachate will be addressed as the “soil/leachate system”.

RESULTS AND DISCUSSION

Portneuf Soil

For the band and mixed treatments, there were no differences in the leachate volume between the different CL application rates. This suggests no effect of CL on water holding capacity up to an application rate of 9 tons/acre.

Application of CL decreased $\text{NH}_4\text{-N}$ in leachate of the mixed treatment, and increased total inorganic N in the band treated soil (data not shown). Under both band and mixed application, rate of CL did not influence $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, or inorganic N masses in the soil/leachate system (Table 1). Data suggests that N applied in a band conserved inorganic N in the soil/leachate system more than when mixed. Comparing band and mixed application at each application rate, when CL and N were applied in a band, greater inorganic N mass was in the system compared to when CL and N were mixed into the soil (Figure 1). Averaged over CL application rates (minus the control), inorganic N mass in the soil/leachate system was 109% greater when N was applied in a band then when mixed. Differences between the two application methods were possibly due to a greater rate of NH_4^+ adsorption as previously mentioned, or due to microbial immobilization and denitrification when N was mixed. Protecting $\text{NH}_4\text{-N}$ in the CL matrix could have reduced the effects of nitrifying and denitrifying microorganisms, or microorganisms simply utilizing $\text{NH}_4\text{-N}$ as a N source. Although organic N analysis of the soil showed no indication of greater microbial immobilization in this study (data not shown), other studies have shown that urea incorporation into soil increases microbial immobilization compared to band applications (Malhi et al., 1995; Lamond and Moyer, 1983). The decreased quantity of inorganic N compared to organic N in the soil likely masked any microbial immobilization effects that could be seen with a total N analysis. Additional research will be needed to determine the influence of microbial immobilization as related to results of this study.

Although microbial immobilization and denitrification were not directly measured, a partial N budget of the soil/leachate system (as shown in Table 4) indirectly lends evidence that denitrification could have influenced differences in $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ masses between application methods. Increased access to and the utilization of the mixed urea-N by microorganisms, and more rapid nitrification were potential reasons for greater microbial immobilization and denitrification (Malhi et al., 1996).

There was likely little loss of urea-N through volatilization as NH_3 in the band or mixed treatments. Research has shown that incorporation of urea into the soil, and precipitation or application of irrigation water to broadcast urea shortly after application at rates as low as 5 mm can greatly reduce or eliminate NH_3 volatilization (Malhi et al., 1996; Fenn and Miyamoto, 1981; Harper et al., 1983). In our study, the urease activity was likely low because the soil was air-dried when urea was applied, the urea was thoroughly mixed into the soil, and 13 mm of water was applied shortly after urea application.

Wolverine Soil

Similar to the Portneuf soil, there were no differences in the leachate volume between the different CL application rates. This suggests that there was no effect of CL on water holding capacity in this soil up to an application rate of 12 tons/acre.

Application of CL increased NO₃-N and total inorganic N of the both application treatments in leachate (data not shown). Under band application, compared to the control, application of CL increased the total inorganic N mass in the soil/leachate system by 35% (Table 1). There was not an influence of CL rate on NO₃-N and NH₄-N masses in the soil/leachate system. Under incorporation application, compared to the control and the lowest CL application rate, applying CL at rates of 6 to 12 tons/acre increased NO₃-N soil/leachate system mass by 21% (Table 1). There was not influence of CL rate on NH₄-N and inorganic N masses in soil/leachate system. Data suggests that N applied in a band may conserve total inorganic N in the soil/leachate system more than when N was mixed. The evidence is not as clear as with the Portneuf soil, but there is a consistent trend for greater total inorganic N in the soil/leachate system when CL is band applied then when mixed. (Figure 1).

REFERENCES

- Bouwmeester, R.J.B., P.L.G. Vlek, and J.M. Stumpe. 1985. Effect of environmental factors on ammonia volatilization from a urea-fertilized soil. *Soil Sci. Soc. Am. J.* 49:376-381.
- Fenn, L.B., and S. Miyamoto. 1981. Ammonia loss and associated reactions of urea in calcareous soils. *Soil Sci. Soc. Am. J.* 45:537-540.
- Harper, L.A., V.R. Catchpole, R. Davis, and K.L. Weir. 1983. Ammonia volatilization: soil, plant and microclimate effects on diurnal and seasonal fluctuations. *Agric. J.* 75:2112-218.
- Huang, Z.T., and A.M. Petrovic. 1994. Clinoptilolite zeolite influence on nitrate leaching and nitrogen use efficiency in simulated sand based golf greens. *J. Environ. Qual.* 23:1190-1194.
- Kithome, M., J.W. Paul, L.M. Lavkulich, and A.A. Bomke. 1998. Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. *Soil Sci. Soc. Am. J.* 62:622-629.
- Lamond, R.E., and J.L. Moyer. 1983. Effects of knifed vs. broadcast fertilizer placement on yield and nutrient uptake by tall fescue. *Soil Sci. Soc. Am. J.* 47:146-149.
- MacKown, C.T. and T.C. Tucker. 1985. Ammonium nitrogen movement in a coarse-textured soil amended with zeolite. *Soil Sci. Soc. Am. J.* 49:235-238.
- Malhi, S.S., M. Nyborg, and J.T. Harapiak. 1995. Recovery of ¹⁵N-labeled fertilizers applied to bromegrass on a Thin Black Chernozem Soil. *Can. J. Soil Sci.* 75:539-542.
- Malhi, S.S., M. Nyborg, and E.D. Solberg. 1996. Influence of source, method of placement and simulated rainfall on the recovery of 15N-labelled fertilizers under zero tillage. *Can. J. Soil Sci.* 76:93-100.
- Ming, D.W., and F.A. Mumpton. 1989. Zeolite in soils. *Minerals in Soil Environments.* p.874-911. *In:* J.B. Dixon and S.B. Week (eds.) SSSA Publisher Inc, Madison, WI.

- Perrin, T.S., J.L. Boettinger, D.T. Drost, and J.M. Norton. 1998. Decreasing nitrogen leaching from a sandy soil with ammonium-loaded clinoptilolite. *J. Environ. Qual.* 27:656-663.
- Prasertsak, P., J.R. Freney, O.T. Denmead, P.G. Saffigna, B.G. Prove, and J.R. Reghenzani. 2002. Effect of fertilizer placement on nitrogen loss from sugarcane in tropical Queensland. *Nutr. Cycl. Agroecosyst.* 62:229-239.
- Williams, P.H., R.J. Tregurtha, and G.S. Francis. 2003. Fate of urea applied to winter spinach in New Zealand. *Nutr. Cycl. Agroecosyst.* 67:245-254.

Table 1. Cumulative NO₃-N, NH₄-N, inorganic N (NO₃-N + NH₄-N) in leachate and soil for Portneuf and Wolverine soils at the end of the study for CL rate and application method treatments.

Soil	CL rate	Band			Mixed		
		NO ₃ -N	NH ₄ -N	NO ₃ -N + NH ₄ -N	NO ₃ -N	NH ₄ -N	NO ₃ -N + NH ₄ -N
	tons/acre	-----lbs/acre-----					
Portneuf	0	77.7	32.0	109.6	61.9	12.5	74.4
	6.7	93.4	71.6	164.9	56.6	17.4	74.0
	13.4	88.8	46.7	135.5	45.2	31.3	76.5
	20.2	88.8	72.7	169.3	61.3	13.6	74.9
	Mean	89.1	55.7	144.9	56.2	18.8	74.9
ANOVA							
CL Rate		NS	NS	NS	NS	NS	NS
Wolverine	0	49.0	40.1	89.2	52.2	46.5	98.7
	6.7	55.6	58.2	113.8	51.4	32.9	84.4
	13.4	60.0	63.9	123.8	61.9	41.3	103.2
	20.2	57.9	66.9	124.8	63.1	38.1	101.3
	26.9	61.0	57.5	118.5	62.3	42.2	104.5
Mean	56.7	57.3	114.0	58.2	40.2	98.4	
ANOVA							
CL Rate		NS	NS	*	*	NS	NS

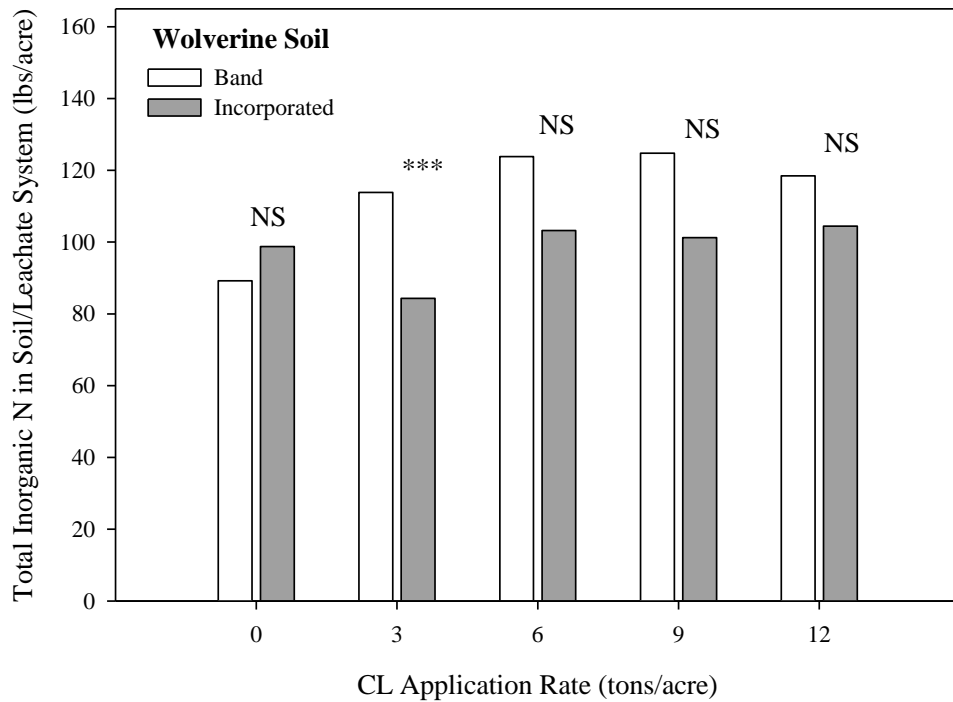
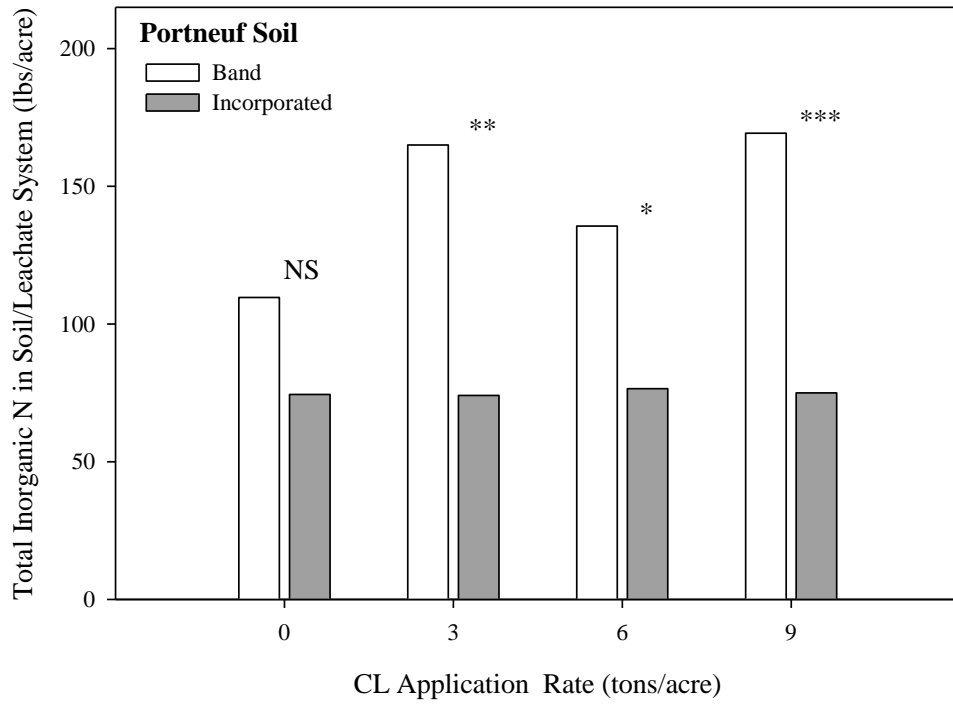


Figure 1. Total inorganic N in soil/leachate systems of Portneuf and Wolverine soils for band and mixed application methods at each CL application rate. Statistical comparisons are between application methods within CL application rates.