

Zeolite Soil Application Method Affects Inorganic Nitrogen, Moisture, and Corn Growth

James Anthony Ippolito, David D. Tarkalson, and Gary A. Lehrsch

Abstract: Adoption of new management techniques that improve soil water storage and soil N plant availability yet limit N leaching may help improve environmental quality. A benchtop study was conducted to determine the influence of a single urea fertilizer rate (224 kg N ha⁻¹) applied with band or fully mixed zeolite (clinoptilolite) application rates (up to 90 Mg ha⁻¹) on NH₄-N and NO₃-N concentrations in a Portneuf silt loam (coarse-silty, mixed, mesic, durinodic Xeric Haplocalcid). Two additional greenhouse experiments were carried out to test the soil moisture status and corn (*Zea mays* L.) growth in a Wolverine sand (mixed, frigid Xeric Torripsamment). Mixing urea fertilizer into silt loam soil resulted in greater urea mineralization as compared with band application of fertilizer + zeolite, and the mixed zeolite was more effective at sorbing and protecting NH₄-N against nitrification. Increasing the rate of mixed zeolite into sandy soil increased the soil moisture content, and mixed zeolite soils contained 1.3% more soil moisture as compared with band zeolite applications. After 6 weeks of corn growth in amended sandy soil, zeolite application at 22 Mg ha⁻¹ seemed to increase corn weight compared with controls. However, increasing zeolite rate up to 90 Mg ha⁻¹ caused a decrease in corn weight, likely caused by the elevated zeolite Na content (3%). Fully mixing zeolite into soil reduced the rate of nitrification likely because of NH₄⁺ adsorption in the zeolite mineral lattice. Thus, mixing zeolite into soil may reduce the leaching of inorganic N. Mixing may also improve the soil water status, although initial leaching of zeolite-borne Na may be necessary before growing crops.

Key words: Sorption, band versus fully mixing, clinoptilolite zeolite, corn, mineralization, nitrification.

(*Soil Sci* 2011;176: 136–142)

Nitrogen (N) leaching losses in agroecosystems increase the potential for human health impacts from contaminated drinking water sources as well as environmental degradation such as water body eutrophication. Hypoxia and anoxia are among the most widespread deleterious anthropogenic influences on estuarine and marine environments (Diaz and Rosenberg, 2008), and these conditions have been suspectedly linked to the use of organic and inorganic N fertilizers. Thus, agricultural systems research leading to management practices that improve N utilization efficiency and decrease N losses is essential (Powlson et al., 2008).

Zeolites can play a role in reducing nonpoint source losses of N. The small molecular size of the open-ringed structure (10⁻⁶–10⁻⁹ m) can physically protect NH₄⁺ ions against microbial nitrification (Ferguson and Pepper, 1987). In a column study, Tarkalson and Ippolito (2010) applied zeolite (0, 6.7, 13.4,

20.2, and 26.9 Mg ha⁻¹) to Portneuf silt loam (Xeric Haplocalcid) and Wolverine sand (Xeric Torripsamment) soils, noting that rates of 6.7 to 13.4 Mg ha⁻¹ conserved inorganic N in both soils. Huang and Petrovic (1994) applied zeolite to sand at a ratio of 1:9 (wt wt⁻¹) and then added increasing amounts of N (0, 98, 196, 293 kg N as [NH₄]₂SO₄). Regardless of N application rate, zeolite reduced both NH₄-N and NO₃-N leaching, likely because of NH₄⁺ retention. In a column study, Zwillingmann et al. (2009) used a sandy soil (Regosol) from Western Australia and demonstrated that 8 g zeolite kg⁻¹ (~18 Mg ha⁻¹) reduced NH₄-N leaching losses by 66%. Application of zeolite at 15 g kg⁻¹ (~34 Mg ha⁻¹) + 200 mg N kg⁻¹ to a Riviera fine sand (Arenic Glossaqualf) significantly reduced NH₃ volatilization as compared with fertilized soil alone, and zeolite-treated soil seemed to maintain greater NH₄-N concentrations (He et al., 2002). In comparison, Weber et al. (1983) noted that zeolite reduced NH₄-N leaching in a Nunn clay loam (Aridic Argiustoll) only at a high application rate (135 Mg ha⁻¹) compared with an unamended control. Thus, lower zeolite application rates may influence coarse-textured soils to a greater degree than fine-textured soils probably because of a significant change in cation exchange capacity (CEC).

Zeolites exhibit a CEC of between approximately 100 and 200 cmol_c kg⁻¹ (Barbarick and Pirela, 1984). MacKown and Tucker (1985) showed that increasing zeolite application rates (0, 28, 56, and 112 Mg ha⁻¹) increased a Rositas loamy sand (Typic Torripsamment) CEC and, thus, enhanced NH₄⁺ retention. Penn et al. (2010) performed batch experiments with zeolite alone (i.e., no soil), noting that NH₄-N sorption was mostly exchangeable as 81% to 87% of zeolite-bound NH₄-N was removed with 1 M KCl. Kithome et al. (1998) made a similar observation, further suggesting that NH₄⁺ exchange was also governed by heterogeneous diffusion into zeolite micropores. Watanabe et al. (2005) described NH₄⁺ adsorption by zeolite using a Langmuir isotherm, suggesting that as more sites in zeolite are filled with NH₄⁺, it becomes increasingly difficult for other solute molecules to find a vacant site. The authors concluded that factors influencing NH₄⁺ sorption include initial NH₄⁺ solute concentration, reaction time, zeolite pore structure and size, and zeolite CEC.

Adoption of new management techniques, such as zeolite utilization, which maximize N use efficiency and water use efficiency may decrease the environmental impact of agriculture (Hatfield and Prueger, 2004). Using rainfall simulators, Xiubin and Zhanbin (2001) showed that zeolites could increase infiltration into a calcareous loess by 7% to 30% on slopes of 5 to 10 degrees and by 50% on 20-degree slopes as compared with untreated soil, but the authors did not specify the zeolite application rate. Bigelow et al. (2001) amended putting green sand with 10% zeolite, noting faster creeping bentgrass (*Agrostis stolonifera* v. *palustris* Huds. Farw.) establishment as compared with unamended putting greens. The authors attributed the findings to increased CEC and greater water retention. Al-Busaidi et al. (2008) applied zeolite to sand at rates equivalent to 0, 1, and 5 kg m⁻², noting an increase in soil water content associated with increasing zeolite rate. In a Bermudagrass (*Cynodon dactylon* [L.] Pers. X. C. *transvallensis* Burt Davy) pot study, Miller (2000) applied four

USDA-ARS Northwest Irrigation and Soils Research Laboratory, Kimberly, ID 83341. Dr. James Anthony Ippolito is corresponding author. E-mail: jim.ippolito@ars.usda.gov

Received October 20, 2010.

Accepted for publication January 3, 2011.

Copyright © 2011 by Lippincott Williams & Wilkins

ISSN: 0038-075X

DOI: 10.1097/SS.0b013e31820e4063

different zeolites to sand at rates of 8.5% by weight, noting that zeolites increased transpirational water by 1% to 16% compared with unamended sand.

Research regarding the use of zeolites with N fertilizer in the U.S. Pacific Northwest is lacking. Therefore, the objectives of the current project were to determine the effect of clinoptilolite zeolite on soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ retention, soil moisture content, and corn growth in two common Pacific Northwest soils.

MATERIALS AND METHODS

Soils and Zeolite

A Portneuf silt loam (coarse-silty, mixed, superactive, mesic Durinodic Xeric Haplocalcid) was collected from a depth of 0 to 30 cm in an agricultural field at the USDA-ARS Northwest Irrigation and Soils Research Laboratory in Kimberly, Idaho. A Wolverine sand (mixed, frigid Xeric Torripsamment) was collected from a depth of 0 to 30 cm in an agricultural field near Firth, Idaho. Both soils are found in row crop production areas. The Portneuf soil is extensive in southern Idaho, occupying approximately 117,000 ha (USDA-NRCS, 2008). The Wolverine soil is primarily located in southern Idaho and Oregon and occupies approximately 11,000 ha (USDA-NRCS, 2008). Although the Wolverine soil is not as extensive as the Portneuf soil, soils similar to the Wolverine series (Xeric Torripsamments) occupy approximately 5 million hectares in the western United States (USDA-NRCS, 2008).

After collection, the soils were air-dried and passed through a 5-mm sieve before analysis. Soil nitrate-N ($\text{NO}_3\text{-N}$) and ammonium-N ($\text{NH}_4\text{-N}$) concentrations were determined using a 2 M KCl extract (Mulvaney, 1996). The Portneuf soil contained 25.2 kg $\text{NO}_3\text{-N ha}^{-1}$ and 7.9 kg $\text{NH}_4\text{-N ha}^{-1}$. The CEC of the uppermost 30 cm of the Portneuf soil is 12.8 cmol(+) kg^{-1} (USDA-NRCS, 2009). The Wolverine soil contained 10.5 kg $\text{NO}_3\text{-N ha}^{-1}$ and 1.1 kg $\text{NH}_4\text{-N ha}^{-1}$. The CEC of the uppermost 30 cm of the Wolverine soil is 4.5 cmol(+) kg^{-1} (USDA-NRCS, 2009).

Clinoptilolite zeolite was obtained from the Zeocorp LLC-owned mine located near Hines, Oregon. A 0.85- to 1.2-mm particle size of zeolite was used in all studies. Additional zeolite properties are found in Table 1. All analyses were provided by Resource Development, Inc. (Wheat Ridge, CO).

TABLE 1. Selected Properties of Clinoptilolite Zeolite Used in the Study

Property	Quantity
CEC, cmol(+) kg^{-1}	155
Charge density, cmol(+) A^{-2}	10.1e^{-23}
Bulk density, g cm^{-3}	0.76
pH	7.5–8.0
Pore size, nm	0.5
Pore volume, %	51
Permeability, m s^{-1}	10^{-3}
Si, %	31.9
Al, %	6.09
Na, %	3.03
K, %	2.77
Fe, %	1.12
Ca, %	0.29
Mg, %	0.26
$\text{NH}_4\text{-N}$, mg kg^{-1}	6.1
$\text{NO}_3\text{-N}$, mg kg^{-1}	2.2

Incubation Study

The effect of banding or fully mixing zeolite with N fertilizer with regard to N dynamics was investigated during a 35-day soil incubation study. Treatments consistent of an equivalent of 224 kg ha^{-1} of N (supplied as urea) applied with an equivalent of 0, 6.7, 13.4, or 20.2 Mg zeolite ha^{-1} . All N + zeolite treatments were weighed and premixed before use. For the banding treatment, 250 g of Portneuf soil was placed in an 8- cm^3 plastic pot, the N + zeolite treatment was placed on the soil surface, and then 250 g of Portneuf soil was placed on top. For the fully mixed treatment, 500 g of Portneuf soil was placed in a 3.78-L plastic bucket, the N + zeolite treatment was added, fully mixed by hand, and then the mixture was placed into the pot. Pots were lined with a plastic liner to prevent leaching, placed in a growth chamber set at 22°C and 30% humidity, and watered twice per week with reverse osmosis water to 80% of field capacity. Pots were destructively sampled on days 1, 4, 7, 14, 21, 28, and 35 and analyzed for $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ (Mulvaney, 1996).

Soil Moisture Study

The effect of banding or fully mixing zeolite with N fertilizer on soil moisture content was investigated during a period of 6 weeks. Treatments were identical to the incubation study except that a 44.8-Mg ha^{-1} zeolite rate was also included. Ten replicates of all treatments were used. The Wolverine soil was used because of its sandy nature and thus poor water-holding capacity. Pots were lined with several layers of paper towels to hold the soil but allow for free drainage. Pots were brought to saturation once per week, allowed to freely drain, and then weighed everyday for the next 7 days to determine the soil moisture content. The process was repeated for 6 weeks at the point which paper towels were disintegrating, with data collected during weeks 1, 2, and 6.

After the 6-week study had concluded, water retention was measured for the mixed zeolite treatments at rates of 0, 13.4, and 44.8 Mg ha^{-1} . To do so, we randomly selected six of the soil moisture study's 10 replications. Soil from these pots was first moistened with de-aired tap water to a water content of 5% by weight, then packed by tamping to a nominal dry bulk density of 1.4 kg m^{-3} into brass rings 19 mm high and 48 mm in diameter. Thereafter, we used a pressure plate extractor to measure water retention at matric potentials of 0, -10, -33, -100, and -300 kPa (Dane and Hopmans, 2002; Reynolds and Topp, 2008). Water retention was measured in a constant room temperature to minimize changing temperature effects on soil water characteristics (Bachmann et al., 2002).

Corn Growth Study as Affected by Soil Moisture

The effect of fully mixing zeolite into soil and varying evapotranspiration (ET) percentages was determined by growing corn (*Zea mays* L.). Based on the previous soil moisture study results, zeolite rates of 0, 22.4, 44.8, or 89.6 Mg ha^{-1} were fully mixed with 3 kg of Wolverine soil (wt:wt basis) and then placed in 20-cm tall \times 20-cm diameter pots with no drain holes. Eight corn seeds were planted per pot, and pots were irrigated daily with tap water to maintain 80% field capacity. After 2 weeks of growth, all pots were thinned to six plants per pot. After thinning, pots were irrigated every 3 days with tap water to replace 100%, 75%, 50%, 40%, or 30% of the ET loss. A set of four reference pots containing no zeolite were used to determine 100% ET losses each day before irrigating the study pots. Each reference pot was overirrigated, allowed to freely drain, the leachate collected, and the difference between the water added and the water lost because of leaching was used to adjust study pots to appropriate ET percentage. One

week after the imposition of the ET treatments, liquid urea was added to all pots to supply 168 kg N ha^{-1} . Two, 4, and 6 weeks after the initiation of the ET treatments, two plants per pot were removed at 2.54 cm above the soil surface, placed in paper bags, dried at 60°C for 72 h, and then the biomass was determined.

Statistics

An analysis of variance to compare zeolite application rates for each application method and to compare application methods was performed using Proc GLM model in SAS (SAS Institute, Inc., 2008) with a significance level (α) of 0.05. Means were separated using the Tukey studentized range test.

RESULTS AND DISCUSSION

Portneuf Soil: Effect of Zeolite on $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$

The effect of increasing band or mixed zeolite rate, applied with a constant N fertilizer rate, on Portneuf soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations during 35 days is presented in Table 2. Few differences existed with increasing band or mixed zeolite rate for $\text{NO}_3\text{-N}$ during 35 days and for $\text{NH}_4\text{-N}$ up to Day 14. Increasing zeolite application, regardless of band or mixed, caused an increase in the soil $\text{NH}_4\text{-N}$ concentration at Days 21 and 28. The increase in $\text{NH}_4\text{-N}$ at these time steps could have been caused by sorption in the zeolite lattice in the presence of greater zeolite quantities. This finding supports that of others

(Ferguson and Pepper, 1987; MacKown and Tucker, 1985; Weber et al., 1983) who showed that zeolite can help retain NH_4^+ in soils. The result seemed to be short-term, as the $\text{NH}_4\text{-N}$ concentration decreased dramatically by Day 35. Most of the NH_4^+ adsorbed onto zeolite inner channels was likely released and quickly nitrified, a mechanism suggested by Perrin et al. (1998).

Compared with band, Portneuf soil receiving mixed zeolite contained greater $\text{NH}_4\text{-N}$ and less $\text{NO}_3\text{-N}$ at Days 7 and 14 and less $\text{NH}_4\text{-N}$ at Day 35. It seemed that mixing urea fertilizer into soil resulted in greater urea mineralization at Days 7 and 14, but the mixed zeolite was more effective at adsorbing $\text{NH}_4\text{-N}$ and protecting it against nitrification. This observation is similar to that found by Tarkalson and Ippolito (2010), who studied band versus mixed zeolite + fertilizer applications to the Portneuf soil in a column leaching study. The authors found that when N fertilizer (224 kg N ha^{-1}) and zeolite (0, 6.7, 13.4, and 20.2 Mg ha^{-1}) were fully mixed into soil, less $\text{NH}_4\text{-N}$ was leached as compared with a control, regardless of zeolite application rate. MacKown and Tucker (1985) mixed increasing amounts of zeolite (an equivalent of 0, 28, 56, and 112 Mg ha^{-1}) into a sandy soil, then added an $(\text{NH}_4)_2\text{SO}_4$ solution, followed by leaching with deionized water. They detected a decrease in leachate NH_4^+ and an increase in soil NH_4^+ associated with increasing zeolite application rates, attributing the findings to an increase in CEC. Zeolite applied in our system also likely increased Portneuf soil CEC because the zeolite CEC was $155 \text{ cmol}(+) \text{ kg}^{-1}$ (Table 1). Zeolite application rates equivalent to 6.7, 13.4, and 20.2 Mg ha^{-1} should have increased the

TABLE 2. Effect of Clinoptilolite Zeolite Rate and Application Method on Mean ($n = 4$) $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ Concentrations at Various Time Intervals for the Portneuf soil

Zeolite Rate [†]	Band/ Mixed	Days						
		1	4	7	14	21	28	35
		----- $\text{NH}_4\text{-N, mg kg}^{-1}$ -----						
0	Band	26.0 (3.6)	54.4 (3.6)a	78.9 (13.8)	17.6 (5.1)a	0.5 (0.1)a	0.6 (0.0)a	0.7 (0.2)a
6.7	Band	26.3 (3.2)	89.5 (15.6)ab	78.1 (212.3)	35.8 (6.8)ab	2.7 (0.9)ab	1.1 (0.2)ab	0.9 (0.1)a
13.4	Band	31.2 (1.7)	66.0 (7.1)ab	66.3 (8.3)	37.5 (5.1)ab	7.1 (1.2)bcd	2.5 (0.3)ab	1.5 (0.2)a
20.2	Band	30.6 (0.9)	95.7 (5.7)b	63.1 (6.8)	30.7 (4.3)ab	10.5 (2.0)cd	6.1 (0.9)c	4.3 (0.8)b
0	Mixed	29.3 (2.3)	78.8 (5.2)ab	84.5 (3.7)	44.4 (3.9)ab	5.5 (1.8)abc	0.6 (0.1)a	0.3 (0.0)a
6.7	Mixed	29.4 (1.0)	76.7 (8.3)ab	109.8 (3.2)	53.3 (10.8)b	6.3 (1.2)abcd	0.9 (0.1)ab	0.6 (0.2)a
13.4	Mixed	34.4 (2.2)	84.2 (6.6)ab	78.4 (14.2)	55.2 (7.6)b	9.4 (1.5)cd	1.6 (0.1)ab	0.6 (0.1)a
20.2	Mixed	31.7 (3.7)	82.0 (8.6)ab	76.8 (7.6)	41.9 (6.3)ab	11.7 (0.5)d	3.0 (0.9)b	0.9 (0.4)a
		-----P > F-----						
Band vs mixed		0.225	0.729	0.036	0.012	0.133	0.103	0.009
		----- $\text{NO}_3\text{-N, mg kg}^{-1}$ -----						
0	Band	6.2 (1.1)	10.3 (0.7)	14.0 (0.5)y	72.3 (4.7)yz	89.8 (4.5)z	77.4 (3.3)z	89.6 (2.8)z
6.7	Band	5.7 (1.2)	10.2 (0.4)	13.9 (0.9)y	76.4 (3.0)yz	97.4 (4.8)yz	101.5 (2.5)y	126.5 (13.4)y
13.4	Band	7.6 (1.3)	8.8 (0.8)	13.5 (0.9)yz	71.8 (3.0)yz	102.4 (7.7)yz	100.3 (5.4)y	117.1 (3.7)y
20.2	Band	6.2 (0.8)	11.4 (0.9)	13.8 (0.7)y	82.6 (8.5)y	106.0 (5.8)yz	98.0 (2.8)y	102.8 (4.2)yz
0	Mixed	4.4 (1.2)	8.8 (0.2)	11.6 (0.5)yz	63.6 (1.1)yz	107.4 (2.1)yz	98.2 (2.4)y	111.8 (4.3)yz
6.7	Mixed	5.0 (0.3)	10.3 (0.5)	12.4 (0.8)yz	64.3 (4.0)yz	114.5 (2.5)y	102.2 (1.8)y	114.2 (1.8)yz
13.4	Mixed	6.8 (0.8)	10.6 (0.8)	11.2 (0.8)yz	56.5 (7.5)z	104.8 (1.0)yz	101.9 (2.6)y	115.6 (1.1)y
20.2	Mixed	6.2 (1.4)	9.0 (0.6)	10.2 (0.4)z	63.6 (3.4)yz	105.7 (2.6)yz	100.4 (2.3)y	116.8 (1.5)y
		-----P > F-----						
Band vs mixed		0.576	0.804	<0.001	0.002	0.108	0.512	0.993

Values inside parentheses represent SEM. Similar lowercase letters within a column, for a particular constituent, represents no significant difference at $\alpha = 0.05$, as determined by the Tukey studentized range test.

[†]All treatments received 224 kg N ha^{-1} urea either banded or fully mixed with clinoptilolite.

Portneuf soil CEC from 12.8 cmol(+) kg⁻¹ (USDA-NRCS, 2009) to 13.3, 13.7, and 14.2 cmol(+) kg⁻¹, respectively.

Wolverine Soil: Effects of Zeolite on Soil Moisture and Corn Growth

Realizing that the greatest changes in soil moisture contents would likely be observed in coarse-textured soils, the Wolverine sand was used for the remaining experiments. The effect of zeolite rate and application method on average soil moisture content at Weeks 1, 2, and 6 are presented in Fig. 1A through F.

In general, increasing the mixed zeolite application rate increased soil moisture content on all days of Weeks 1, 2, and 6, whereas the opposite effect was observed for band zeolite application. Where zeolite was banded, the relatively low matric potentials in the fine-textured zeolite band (or layer) led to a potential gradient that caused water to flow from the overlying coarse-textured Wolverine sand into deeper layers, thus decreasing soil water contents in the upper sampled layers. The mixed zeolite application increased soil moisture by 1.3% (weight basis) on average as compared with band zeolite

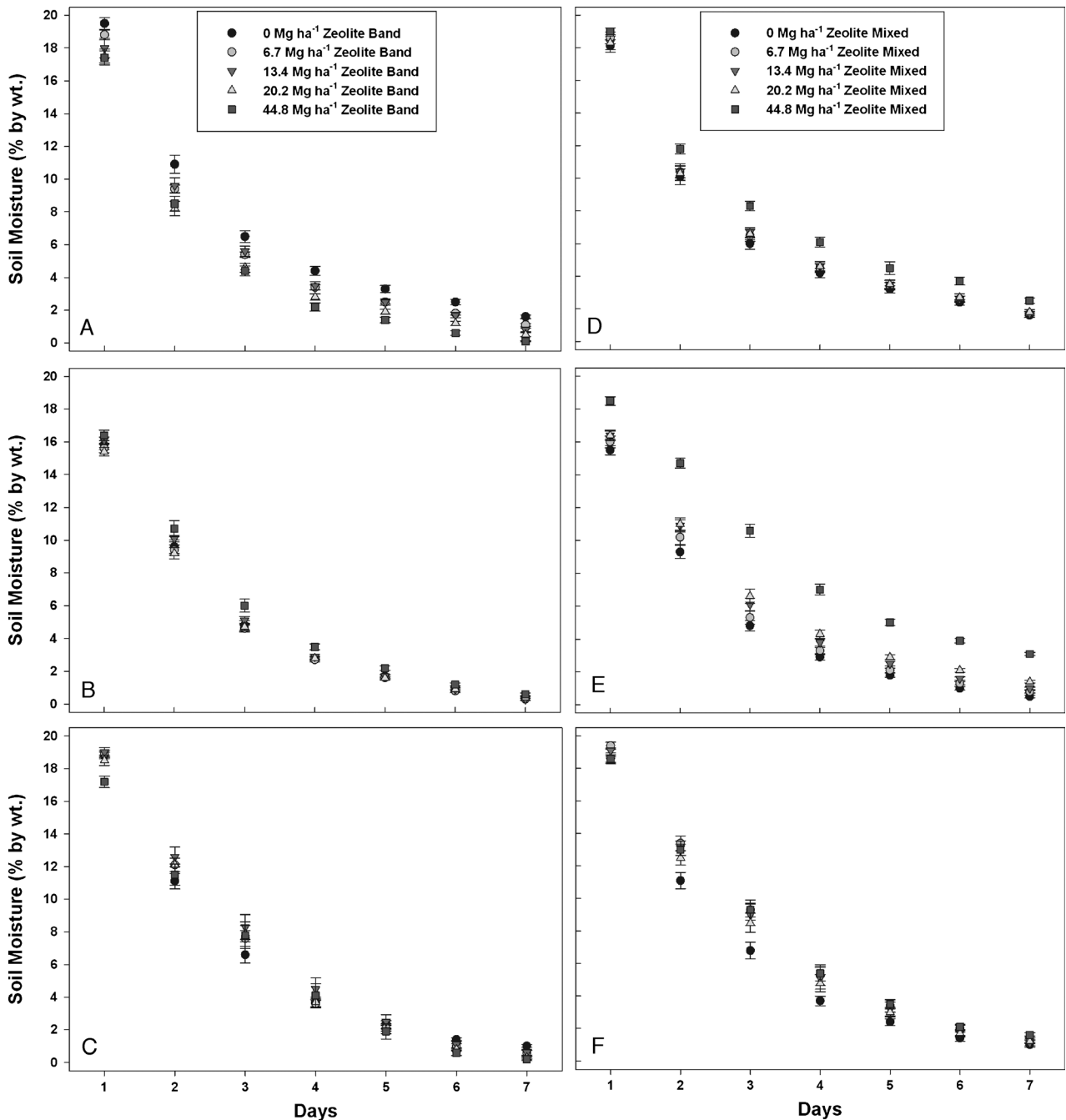


FIG. 1. Wolverine sand mean (*n* = 10) percent soil moisture (weight basis) at Week 1 (A), Week 2 (B), and Week 6 (C) caused by increasing zeolite band rates or at Week 1 (D), Week 2 (E), and Week 6 (F) caused by increasing mixed zeolite rates days after saturation. Error bars represent SEM.

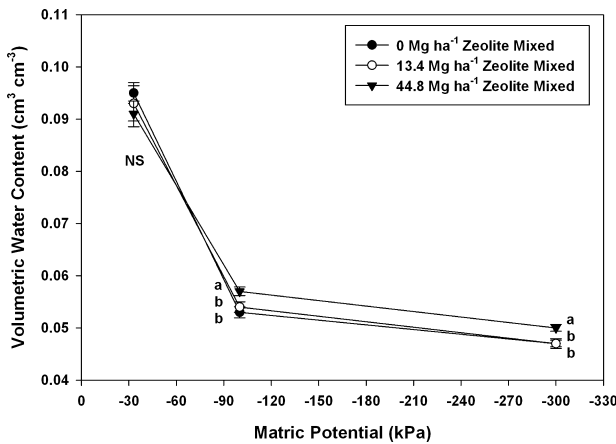


FIG. 2. Mean ($n = 6$) volumetric water content of the Wolverine sand collected at Week 6 after mixed zeolite application of 0, 13.4, or 44.8 Mg ha^{-1} . At each matric potential, data points denoted with a common letter are not significantly different at $\alpha = 0.05$ as determined by the Tukey studentized range test. Error bars represent SEM. NS: no significant differences among zeolite rates within a matric potential.

application over all weeks. At most time steps, the 44.8 Mg ha^{-1} mixed zeolite application rate contained the most water, and a comparable band application contained 2.6% less soil moisture on average; the 44 Mg ha^{-1} mixed zeolite application also contained 2.1% more water than the 0 Mg ha^{-1} mixed control.

The effects on water retention of increasing rates of zeolite mixed with Wolverine sand was also determined (Fig. 2). Because differences among rates were minimal at potentials of 0 and -10 kPa, those data are not reported. In contrast, soil samples that had been amended with 44.8 $\text{Mg zeolite ha}^{-1}$ retained more water at potentials of -100 and -300 kPa than did the control or samples amended with 13.4 $\text{Mg zeolite ha}^{-1}$. This finding reveals that more water was being retained in the pore spaces of the 44.8- Mg ha^{-1} zeolite mixed with Wolverine sand, thus improving this coarse-textured soil's potential to support crop growth.

Other researchers have also found water retention or soil water contents to be greater in soils to which zeolite was applied. Bigelow et al. (2001) mixed 10% zeolite with putting green sand and noted a 20% increase in volumetric water content during the first year after putting green establishment as compared with unamended sand; no difference was observed during Year 2 of the study. Al-Busaidi et al. (2008) applied zeolite to sand at a rate of 5 kg m^{-2} (5% by weight), reporting an increase in soil water content of approximately 2.5% to 4.8% (by weight), depending on water source, as compared with a control. After establishing Bermudagrass in sand, Miller (2000) replaced a plug of soil with one of four different zeolites applied at a rate of 8.5% by weight. The author noted that zeolites increased transpirational water (the volumetric water content where the daily transpiration rate of drought-stressed plants become less than 12% of well-watered plants) by 1% to 16% over sand alone. Nus and Brauen (1991), who applied increasing zeolite rates (5%, 10%, and 20% vol:vol) to sand, found an increase in volumetric water content when measured at -10 kPa; volumetric water content at other tensions was not determined.

Because mixed zeolite applications increased soil moisture content as compared with band zeolite applications, mixed zeolite application effects on corn growth as a function of soil moisture were studied next. Specifically, corn growth as a

function of mixed zeolite application rates and ET replenishment rate, with time, is presented in Fig. 3. Decreasing ET replenishment rate decreased corn growth at 2 (Fig. 3A), 4 (Fig. 3B), and 6 (Fig. 3C) weeks after imposing ET treatment. All ET replenishment rates were different from one another except the 75% and 100% treatments at Week 4; the ET by zeolite interaction was not significant at any period. Within an ET replenishment rate at each time, increasing zeolite application rate

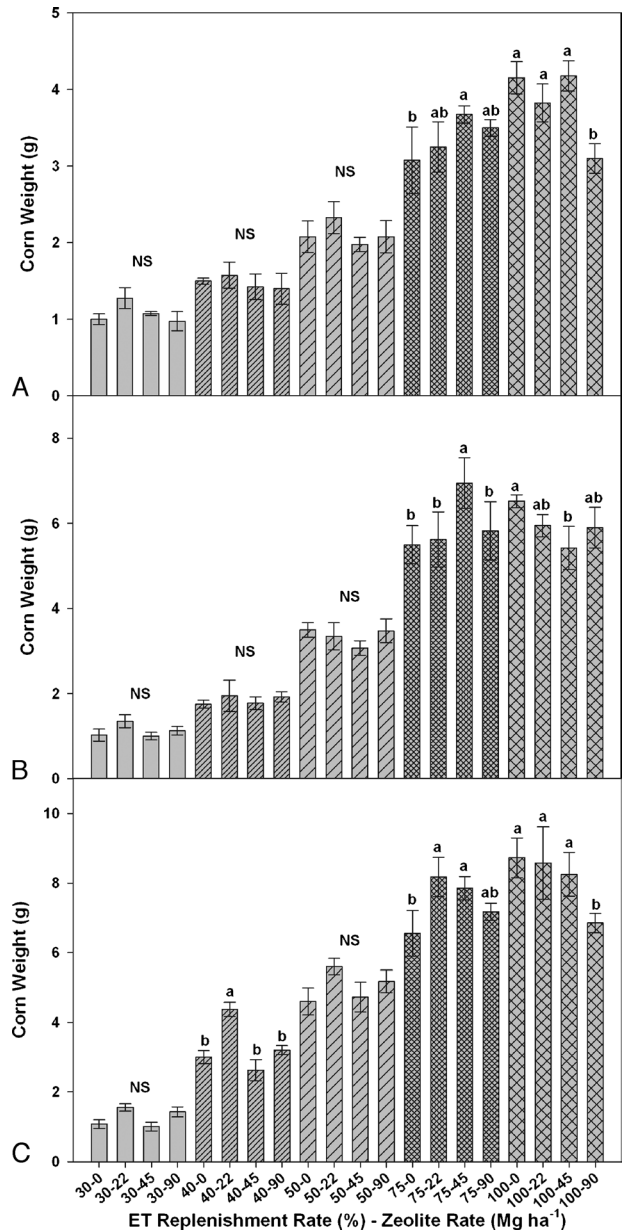


FIG. 3. Mean ($n = 4$) corn dry weight as affected by percent evapotranspiration replenishment rate (ET) and mixed zeolite application rate at 2 (A), 4 (B), and 6 (C) weeks after imposition of ET replenishment rates. Within an ET replenishment rate at each 2-week interval, bars denoted with a common letter are not significantly different at $\alpha = 0.05$ as determined by the Tukey studentized range test. Error bars represent SEM. NS: no significant differences among zeolite rates with an ET replenishment rate and measurement time.

effects on corn growth were inconsistent. When averaged across all ET replenishment rates, however, at Week 6, increasing zeolite application rate from 22 to 90 Mg ha⁻¹ caused a decrease in corn growth.

Based on our previous soil moisture study, it was assumed that mixing greater rates of zeolite into a sandy soil would help offset reduced plant growth under moisture stress; obviously, this was not the case. Similarly, Jayasinghe et al. (2008) mixed zeolite with oil palm waste at ratios of 1:3 and 1:10 and studied the growth of lettuce (*Lactuca sativa* L.) throughout a 7-week period. The authors showed that shoot and root fresh and dry weights and number of leaves per plant increased with the 1:10 compared with the 1:3 zeolite:palm oil waste mixture. Although not discussed, the effect must have been zeolite related because the lettuce nutrient content was similar between treatments. Kavooosi (2007) noted an apparent decrease in rice (*Oryza sativa*) grain yield with increasing zeolite application (8, 16, and 24 Mg ha⁻¹). Ferguson et al. (1986) found that creeping bentgrass establishment decreased as zeolite application rate increased by 5% to 10% (by volume), associating the decrease with zeolite sodium content. This could explain the observed decrease in corn weight with increasing zeolite application at Week 6 and possibly results from previous studies. Zeolite used by Ferguson et al. (1986) contained approximately 3% Na, similar to that in the zeolite we used, and they applied zeolite at approximately 158 and 315 Mg ha⁻¹, much greater than we applied. The authors noted that Na was leached from the system after 1 year and would have been expected to leach in our system if we had permitted free drainage to occur.

CONCLUSIONS

We examined the effect of clinoptilolite zeolite application on typical agricultural soils of the U.S. Pacific Northwest. Compared with a band application, fully mixing up to 20.2 Mg ha⁻¹ of zeolite into a Portneuf silt loam protected NH₄⁺ against nitrification. This was likely caused by an increase in CEC and subsequent adsorption of NH₄⁺ in the zeolite mineral lattice. Mixing zeolite into a Wolverine sand at 44.8 Mg ha⁻¹ increased soil moisture by 2.6% and 2.1% (by weight) as compared with a band application of 44.8 Mg ha⁻¹ or a control, respectively. Overall, as compared with band application, fully mixing up to 44.8 Mg ha⁻¹ zeolite into a Wolverine sand improved the soil moisture content by 1.3%. Greater water contents in zeolite-treated than untreated soil were also detected in a supporting study. Water retention at matric potentials of -100 and -300 kPa were greatest for a mixed zeolite rate of 44.8 Mg ha⁻¹ compared with a lower zeolite rate and a control; water at these matric potentials can be considered plant available. Based on these soil moisture studies, it was assumed that mixing greater application rates of zeolite into a Wolverine sand would help offset reduced corn growth under moisture stress; this was not observed. Rather, it seemed that greater mixed zeolite application rates resulted in lower corn weights, likely a result of Na added with the zeolite. Based on the previous results, the use of fully mixing clinoptilolite zeolite into soil can help conserve NH₄⁺, but excess zeolite-borne Na may need to be leached before growing crops.

ACKNOWLEDGMENTS

This study was supported by Zeocorp LLC, CRADA 58-3k95-8-1283. Mention of a specific product or vendor does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture or imply its approval to the exclusion of other products that may be suitable. The authors thank Ms.

Mary Ann Kay and Mr. Jim Foerster for project maintenance and analyses.

REFERENCES

- Al-Busaidi, A., T. Yamamoto, M. Inoue, A. E. Eneji, Y. Mori, and M. Irshad. 2008. Effects of zeolite on soil nutrients and growth of barley following irrigation with saline water. *J. Plant Nutr.* 31:1159–1173.
- Bachmann, J., R. Horton, S. A. Grant, and R. R. Van der Ploeg. 2002. Temperature dependence of water retention curves for wettable and water-repellent soils. *Soil Sci. Soc. Am. J.* 66:44–52.
- Barbarick, K. A., and H. J. Pirela. 1984. Agronomic and horticultural uses of natural zeolites: A review. *In: Zeo-agriculture: Uses of natural zeolite in agriculture and aquaculture.* W. G. Pond, and F. A. Mumpton (eds.). Westview Press, Boulder, CO, pp. 93–103.
- Bigelow, C. A., D. C. Bowman, D. K. Cassel, and T. W. Ruffy, Jr. 2001. Creeping bentgrass response to inorganic soil amendments and mechanically induced subsurface drainage and aeration. *Crop Sci.* 41:797–805.
- Dane, J. H., and J. W. Hopmans. 2002. Pressure plate extractor. *In: Methods of Soil Analysis, Part 4: Physical Methods.* J. H. Dane, and G. C. Topp (eds.). Soil Science Society of America, Madison, WI, pp. 688–690.
- Diaz, R. J., and R. Rosenberg. 2008. Spreading dead zones and consequences for marine ecosystems. *Science* 321:926–929.
- Ferguson, G. A., and I. L. Pepper. 1987. Ammonium retention in sand amended with clinoptilolite. *Soil Sci. Soc. Am. J.* 51:231–234.
- Ferguson, G. A., I. L. Pepper, and W. R. Kneebone. 1986. Growth of creeping bentgrass on a new medium for turfgrass growth: Clinoptilolite zeolite-amended sand. *Agron. J.* 78:1095–1098.
- Hatfield, J. L., and J. H. Prueger. 2004. Nitrogen over-use, under-use, and efficiency. "New directions for a diverse planet." Proceedings of the 4th International Crop Science Congress. Brisbane, Australia, September 26–October 1. Available from: http://www.cropsociety.org.au/icsc2004/plenary/2/140_hatfield.htm (verified July 13, 2010).
- He, Z. L., D. V. Calvert, A. K. Alva, Y. C. Li, and D. J. Banks. 2002. Clinoptilolite zeolite and cellulose amendments to reduce ammonia volatilization in a calcareous sandy soil. *Plant Soil* 247:253–260.
- 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.
- Jayasinghe, G. Y., Y. Tokashiki, M. Kitou, and K. Kinjo. 2008. Oil palm waste and synthetic zeolite: An alternative soil-less growth substrate for lettuce production as a waste management practice. *Waste Manage. Res.* 26:559–565.
- Kavooosi, M. 2007. Effects of zeolite application on rice yield, nitrogen recovery, and nitrogen use efficiency. *Commun. Soil. Sci. Plant Anal.* 38:69–76.
- 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.
- 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.
- Miller, G. L. 2000. Physiological response of bermudagrass grown in soil amendments during drought stress. *HortSci.* 35:213–216.
- Mulvaney, R. L. 1996. Nitrogen: Inorganic forms. *In: Methods of Soil Analysis, Part 3: Chemical Methods.* D. L. Sparks (ed.). Soil Science Society of America, Madison, WI, pp. 1123–1184.
- Nus, J. L., and S. E. Brauen. 1991. Clinoptilolite zeolite as an amendment for establishment of creeping bentgrass on sandy media. *HortSci.* 26:117–119.
- Penn, C. J., J. G. Warren, and S. Smith. 2010. Maximizing ammonium nitrogen removal from solution using different zeolites. *J. Environ. Qual.* 39:1478–1485.

- Perrin, T. S., J. L. Boettinger, D. T. Drost, and J. M. Norton. 1998. Decreasing nitrogen leaching from sandy soil with ammonium-loaded clinoptilolite. *J. Environ. Qual.* 27:656–663.
- Powlson, D. S., T. M. Addiscott, N. Benjamin, K. G. Cassman, T. M. de Kok, H. van Grinsven, J. L. L'hirondel, A. A. Avery, and C. van Kessel. 2008. When does nitrate become a risk for humans? *J. Environ. Qual.* 37:291–295.
- Reynolds, W. D., and G. C. Topp. 2008. Soil water desorption and imbibition: Tension and pressure techniques. *In: Soil Sampling and Methods of Analysis*, 2nd Ed. M. R. Carter, and E. G. Gregorich (eds.). CRC Press, Boca Raton, FL, pp. 981–997.
- SAS Institute. 2008. SAS/STAT User's Guide. Version 9.2. SAS Institute, Cary, NC.
- Tarkalson, D. D., and J. A. Ippolito. 2010. Clinoptilolite zeolite influence on inorganic nitrogen in silt loam and sandy agricultural soils. *Soil Sci.* 175:357–362.
- USDA-NRCS. 2008. Soil Extent Mapping Tool [Online]. Available from: <http://www.cei.psu.edu/soiltool/semtool.html> (verified July 13, 2010).
- USDA-NRCS. 2009. Web Soil Survey [Online]. Available from: <http://websoilsurvey.nrcs.usda.gov/app/HomePage.htm> (verified July 13, 2010).
- Watanabe, Y., H. Yamada, J. Tanaka, Y. Komatsu, and Y. Moriyoshi. 2005. Ammonium ion exchange of synthetic zeolites: The effect of their open-window sizes, pore structures, and cation exchange capacities. *Sep. Sci. Technol.* 39:2091–2104.
- Weber, M. A., K. A. Barbarick, and D. G. Westfall. 1983. Ammonium adsorption by a zeolite in a static and a dynamic system. *J. Environ. Qual.* 12:549–552.
- Xiubin, H., and H. Zhanbin. 2001. Zeolite application for enhancing water infiltration and retention in loess soil. *Resour. Conserv. Recycl.* 34:45–52.
- Zwingmann, N., B. Singh, I. D. R. Mackinnon, and R. J. Gilkes. 2009. Zeolite from alkali modified kaolin increases NH_4^+ retention by sandy soil: Column experiments. *Appl. Clay Sci.* 46:7–12.