

Article

Effects of Zeolitic Urea on Nitrogen Leaching ($\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$) and Volatilization (NH_3) in Spodosols and Alfisols

Ayaz Ahmad ^{1,2}, Shahzada Sohail Ijaz ² and Zhenli He ^{1,*} 

¹ Indian River Research and Education Center, Department of Soil and Water Sciences, Institute of Food and Agricultural Sciences, University of Florida, 2199 S. Rock Rd., Fort Pierce, FL 34945, USA; ayaz1432@gmail.com

² Institute of Soil Science, Pir Mehr Ali Shah Arid Agriculture University Rawalpindi, Murree Road, Rawalpindi 46300, Pakistan; shahzadasohail@uaar.edu.pk

* Correspondence: zhe@ufl.edu; Tel.: +1-(772)-971-5854

Abstract: Global use of urea nitrogen (N) fertilizer is increasing, but N losses are still very high (40–70%). Zeolites have the capability of holding NH_4^+ , thus reducing N losses when applied as a soil amendment. However, application of a large quantity of zeolite is costly and inconvenient. In this study, zeolitic fertilizers were evaluated to select the best formulation with reduced leaching of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ and NH_3 volatilization in agricultural soils (Alfisol and Spodosol). The treatments included the following: T_0 = control, T_1 = urea fertilizer, T_2 = zeo-urea (1:1), T_3 = zeo-urea (2:1), T_4 = zeo-urea (3:1), T_5 = zeo-urea (1:2), and T_6 = zeo-urea (1:3). Leaching was performed at 4, 8, 12, 19, 25, 32, 39 and 45 days after the soils were treated with the designated fertilizers, including control, and packed into columns. Leachate samples were collected after each leaching event and analyzed for the concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ and the quantity of leachate. Ammonia volatilization was recorded at days 1, 5, 9, 13 and 20 of soil treatments. Results indicate that zeolitic fertilizer formulations effectively reduced N losses. $\text{NH}_4\text{-N}$ loss was reduced by 13% and 28% by zeo-urea (1:1) in Alfisol and Spodosol soils, respectively, whereas zeo-urea (2:1) and zeo-urea (3:1) effectively decreased $\text{NO}_3\text{-N}$ leaching in Alfisol. Volatilization loss of NH_3 was reduced by 47% in Spodosol and 32% in Alfisol soil with zeo-urea (1:1) as compared with that of urea fertilizer. The results suggest that zeo-urea (1:1) is an effective fertilizer formulation for reducing N losses, especially in Alfisol, as compared with conventional urea fertilizer.



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1. Introduction

The ever-increasing population of the world has put pressure on cultivated land and created a threat to food security [1]. Current production must be increased 25–70% by 2050 to meet the food demands [2]. This situation has compelled the agriculture sector to use excessive fertilizers and pesticides for achieving higher crop yield. However, environmental pollution has become more frequent [3] as a big portion of the applied fertilizers is lost via leaching or volatilization, which results in increased production cost and environmental pollution.

Global nitrogen (N) demand is expected to increase 1.4% per annum up to 2023. Urea is the most commonly used N fertilizer, and world urea demand is estimated to increase 1.2% per annum, leading to 184 Mt in 2023 [4]. Global use of urea has increased more than 100-fold during the last four decades and now constitutes >50% of the global nitrogenous fertilizer usage [5].

Nitrogen losses from urea could be as high as 42% through volatilization or leaching [6]. Urea is hydrolyzed into ammonium in soil, which may be volatilized as ammonia or converted into nitrate through the nitrification process, depending on soil conditions. The agriculture sector is a major source of NH_3 volatilization to the environment, with the

majority coming from applied urea [7]. Average losses in the form of NH₃ may range 20–30% of applied N [8], depending upon soil type, pH, temperature, and soil moisture content. However, leaching loss of N in sandy loam soil under submerged conditions may account for up to 80–84% [9]. In order to reduce N losses from urea, different strategies have been proposed, including proper rate, timing, and placement of the N source [10,11] and use of urease inhibitors, denitrifiers, and stabilized fertilizers. If proper measures are adopted to minimize fertilizer losses, a significant amount of capital can be saved.

The structural and physio-chemical properties of zeolite result in reduced N losses. These are hydrated aluminosilicates that consist of three-dimensional networks of SiO₄ and an AlO₄ tetrahedron linked by oxygen atoms. Si is substituted by Al, resulting in a net negative charge, which is compensated by cations [12]. Similarly, zeolites have high sorption capacity towards ammonium cations [13]. How long zeolites can retain the ammonium cations needs to be determined by leaching experiments. Zeolites have a special importance in agriculture [14]. Sorption of cations and structural channels make zeolites attractive for NH₄⁺ adsorption, leading to reduced N losses [15].

Zeolites are being used as a soil amendment to enhance nutrient use efficiency [16]. Nutrients are retained by the porous minerals when added together with fertilizers. High nutrient use efficiency achieves similar yields with smaller amounts of fertilizers. Zeolites are mainly associated with sorption of NH₄⁺, K⁺, and micro-cation elements [17]. These nutrients are released more slowly from the zeolite in the root zone or retained in the zeolite structure. Zeolites are environmentally friendly because they are compatible with the environment. They reduce leaching losses and enhance crop yield [18,19]. Application of zeolites in sandy loam soil at 9 t/ha reduced N leaching by 36% with urea fertilizer [20]. Similarly, reduced NH₃ volatilization was also reported in incubation studies when zeolites were applied in soil along with fertilizers [21,22]. However, the cost of zeolites for soil amendment is high. The recent mining of zeolite from Pakistan has opened new dimensions for research.

There is a great need to formulate simple and cost effective zeolitic fertilizers. This will not only reduce the costs of zeolite as a soil amendment but also enhance the efficiency of N fertilizer. It is hypothesized that zeolite-based slow-release fertilizers can reduce N losses by volatilization and/or leaching. This study was designed to evaluate the effectiveness of zeolitic urea fertilizers for reducing ammonia volatilization and leaching loss of NH₄-N and NO₃-N in sandy soil. The information can facilitate the development of the optimal zeolitic urea formulations for agricultural applications.

2. Materials and Methods

A column leaching study was conducted at the Indian River Research and Education Centre of the University of Florida-IFAS, USA to examine different formulations of zeolitic urea with respect to their losses of N in the form of NH₄-N, NO₃-N, and NH₃ volatilization.

2.1. Soil Sampling

Two types of soils (Alfisol and Spodosol) at the 0–20 cm depth were collected from McArthur Citrus Grove and University of Florida Research farm in Fort Pierce in the south of Florida. After removal of roots, stones, and other visible materials, soil samples were air-dried, homogenized, and passed through a 2-mm sieve prior to use.

Soil particle composition was determined by particle size analysis [23]. Soil pH was determined at the soil/water ratio of 1:1.25 using a pH meter (Accumet-200 Fisher Scientific, Waltham, MA, USA). Cation exchange capacity was determined following an ammonium acetate method [24]. Organic matter content was calculated by multiplying soil organic carbon by 1.724, with the latter being determined with a combustion method using a C/N analyzer (Vario EL III, Hanau, Germany). Table 1 shows Physio-chemical properties of soil.

Table 1. Physio-chemical properties of soil.

Soil Type	Alfisol (Riviera Series)	Spodosol (Ankona Series)
Sand (%)	83	92
Silt (%)	5	3
Clay (%)	12	5
Texture	Loamy	Sandy
pH	6.1	5.2
CEC (meq/100 g)	15.1	5.7
Organic Matter (g kg^{-1})	18.2	8.3

2.2. Zeolitic Fertilizer Formulations

Natural zeolite mined in Pakistan of clinoptilolite type was obtained from Mehran mining company. It was ground and passed through a 0.250 mm sieve. It was examined for CEC and underwent a spectroscopic study. Spectroscopy was carried out in the wave number range of 500 to 4000 cm by using a FT/IR-6600 type A Fourier Transform Infrared Spectrometer (FTIR). Cation exchange capacity was recorded by following the ammonium acetate method. By weight, twenty parts urea fertilizer and one part water were mixed and heated on a hot plate at 105–115 °C until the fertilizer was completely liquefied. Then, ground zeolite was added at 1:1 ratio by weight to the liquefied mixture and thoroughly mixed for 3 to 4 min. Liquefied material was completely sorbed by zeolite as indicated by the disappearance of liquid from the surface of the mixture. The temperature was lowered to solidify the mixture [25]. Using the same method, other zeolitic urea formulations (2:1, 3:1, 1:2, and 1:3) were prepared by changing the proportion of zeolite and urea fertilizer accordingly. Total N content of zeolitic urea formulations was determined using the C/N analyzer (Table 2).

Table 2. Nitrogen content (%) in zeolitic formulations.

Type of Fertilizer Formulation	Nitrogen Content (%)
Urea	46
Zeo-urea (1:1)	21.60
Zeo-urea (2:1)	14.13
Zeo-urea (3:1)	10.80
Zeo-urea (1:2)	29.20
Zeo-urea (1:3)	34.50

2.3. Column Leaching Experiment

Zeolitic urea formulations were applied to one kilogram of soil for each fertilizer type in plastic bags and mixed thoroughly. The applied N dose was equivalent to 250 kg/ha. Soil without any fertilizer was treated as T₀ and NH₄-N, NO₃-N and NH₃ losses from T₀ (control) were also recorded at each leaching event. The amount of each N compound from the control was then subtracted from all other treatments to highlight the effect of treatments without the interruption from control. Very minute quantities of N compounds were present in these samples. Each treatment was replicated three times. The treatments consisted of the following: T₀ = control, T₁ = urea fertilizer, T₂ = zeo-urea (1:1), T₃ = zeo-urea (2:1), T₄ = zeo-urea (3:1), T₅ = zeo-urea (1:2), and T₆ = zeo-urea (1:3). Soil was packed in Plexiglas columns (30.5 cm length and 6.6 cm inner diameter). One circle of Whatman # 42 filter paper was placed at the bottom and top of each column to prevent soil loss and proper water application. Soil columns were moistened from the bottom in a plastic pan with deionized water until the water holding capacity was reached. After saturation, the deionized water was analyzed to account for N loss.

The columns were placed in a wooden stand and left for 5 days for natural soil compaction. A sponge containing glycerol solution was placed at the top of the columns to measure the volatilized NH₃ by the sponge-trapping and extraction method modified by

He et al. [26]. Trapped NH_3 was extracted with KCl after 1, 5, 9, 13 and 20 days and analyzed using the N/P discrete analyzer (EasyChem Plus, Systea Scientific, Oak Brook, IL, USA). Leachate collected during the compaction process was added to the respective column. Then, 125 mL of deionized water with pH 6.6 was applied through a peristaltic pump and the leachate samples were collected at regular intervals of 4, 8, 12, 19, 25, 32, 39, and 45 days. Intervals for the determination of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and NH_3 were selected on the basis of the N transformations in soil, leaching trends of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$, NH_3 volatilization, quantity of water available for leaching, and number of leaching events. The first leaching event was completed at day 4 so that sufficient zeolitic urea could be hydrolyzed to $\text{NH}_4\text{-N}$ for leaching. However, NH_3 volatilization was recorded after 1 day as volatilization of NH_3 starts just after the application of treatments. The total volume of applied water (1000 mL) was equivalent to half a year's average rainfall in Fort Pierce. Leachate from each column was analyzed using the N/P discrete analyzer for the concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$. At the end of experiment, soil samples were collected from each column, mixed thoroughly, and analyzed for extractable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$.

2.4. Statistical Analysis

Data were subjected to a two-way ANOVA test to evaluate treatment effects using Statistix 10 software. The means of pair-wise treatments were compared by Tukey's Honestly Significance test at 5% level of significance.

3. Results

Cation exchange capacity of the zeolite was recorded as 123 me/100 g. Spectroscopic analysis of zeolite depicted a strong band at $929\text{--}1096\text{ cm}^{-1}$ and $3380\text{--}3502\text{ cm}^{-1}$, indicating the presence of an aluminosilicate lattice of zeolite and a hydroxyl functional group [27] (Figure 1).

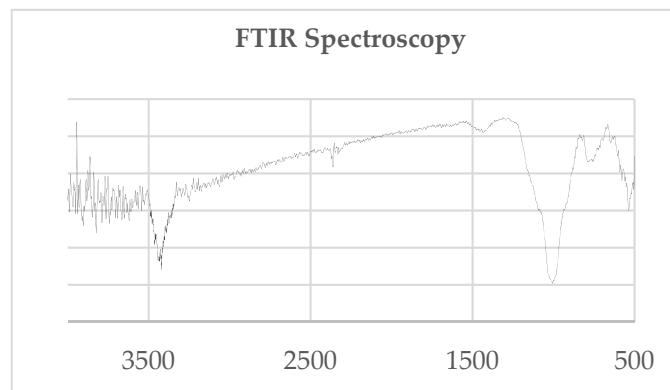


Figure 1. FTIR spectra of zeolite.

3.1. Effect on Ammonium Leaching Loss

The effects of zeolitic fertilizer formulations on ammonium leaching at different leaching events in Alfisol and Spodosol soils were compared with those of urea (Figure 2a,b). The amount of $\text{NH}_4\text{-N}$ in leachate was largest in Alfisol soil treated with urea, as compared to that of all the other treatments at day 8, and it continued to rise in the subsequent leaching events. Leachate ammonium concentration reached to maximum at day 12 with urea and zeo-urea (1:1), while the peak occurred at day 19 with all the other zeolitic formulations, and the concentration showed a decreasing trend afterwards, regardless of treatment (Figure 2a). Similarly, in Spodosol soil leachate, the $\text{NH}_4\text{-N}$ concentration was higher at day 8 with urea than it was with any of the zeolitic formulations. However, after day 8, all the treatments except zeo-urea (1:3) followed a decreasing trend. In both soils, $\text{NH}_4\text{-N}$ losses were little changed from day 32 through 45 for all the treatments (Figure 2b).

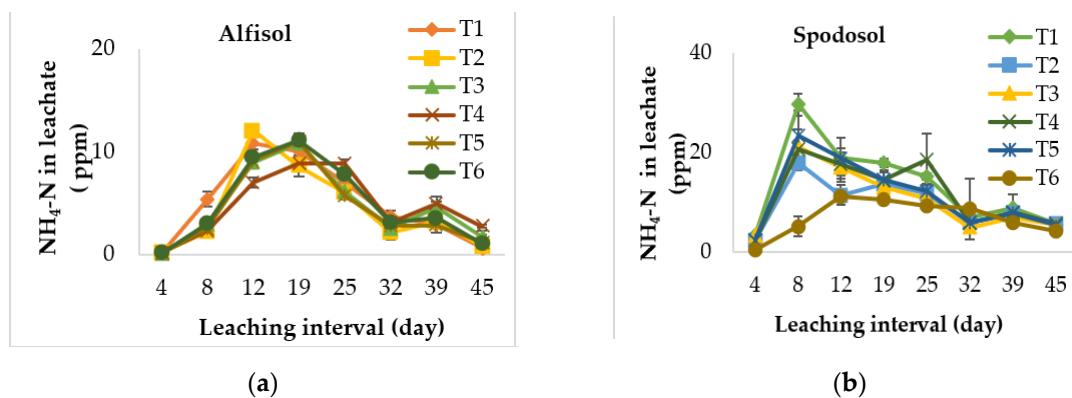


Figure 2. Effects of treatments on $\text{NH}_4\text{-N}$ leaching at different leaching intervals from (a) Alfisol soil and (b) Spodosol soil.

Cumulative amounts of $\text{NH}_4\text{-N}$ measured in leachate during this experiment for Alfisol and Spodosol soils are shown in Figure 3a,b. For Alfisol soil, the maximum $\text{NH}_4\text{-N}$ was lost with urea, though statistically similar to that of zeo-urea (2:1), zeo-urea (3:1), and zeo-urea (1:3). However, a statistically significant reduction in the loss of $\text{NH}_4\text{-N}$ was recorded in the treatments of zeo-urea (1:1) and zeo-urea (1:2) (Figure 3a). Similarly, for Spodosol soil, the maximum loss of $\text{NH}_4\text{-N}$ also occurred with urea, and the treatments of zeo-urea (1:1) and zeo-urea (1:3) significantly reduced the loss of $\text{NH}_4\text{-N}$ in leachate as compared to that of urea (Figure 3b). Therefore, zeo-urea (1:1) proved the most effective treatment to reduce leaching of $\text{NH}_4\text{-N}$ for both Alfisol and Spodosol soils.

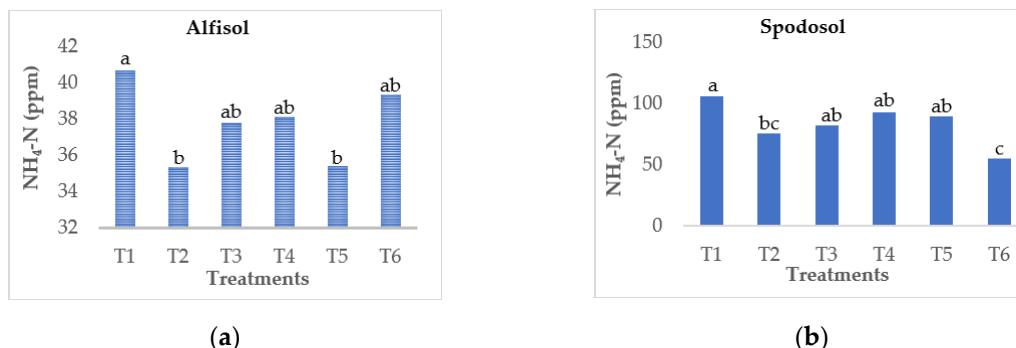


Figure 3. Effect of treatments on cumulative losses of $\text{NH}_4\text{-N}$ from (a) Alfisol soil and (b) Spodosol soil. Means with different letters indicate significant differences among treatments by Tukey's test at $p \leq 0.05$.

3.2. Effect on Nitrate Leaching Loss

The effects of zeolitic fertilizer formulations on nitrate leaching at different leaching events in Alfisol and Spodosol soils are shown in Figure 4a,b. During the first three leaching events, very small amounts of $\text{NO}_3\text{-N}$ were recorded in leachate for Alfisol, regardless of treatment (Figure 4a). However, leachate nitrate concentration increased from day 19 to 39, with a peak value occurring at day 39, and it decreased thereafter for all the treatments. In Spodosol, smaller amounts of $\text{NO}_3\text{-N}$ were recorded in leachate, which could be due to a weaker nitrification. Statistically, no significant differences among the treatments were observed in $\text{NO}_3\text{-N}$ leaching from Spodosol soil (Figure 4b).

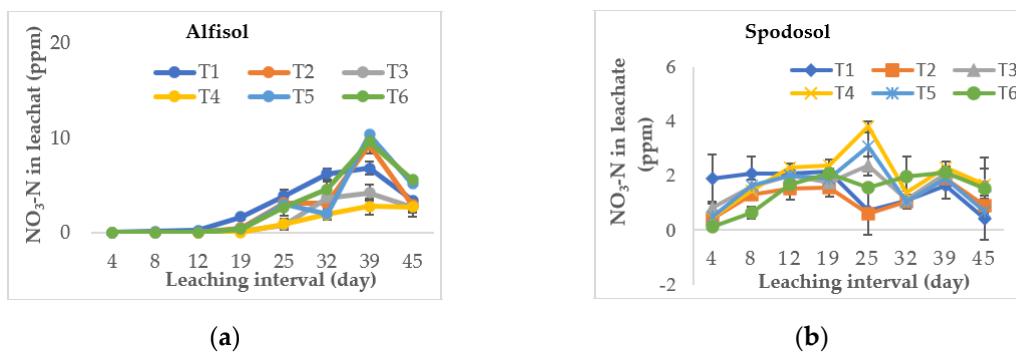


Figure 4. Effect of treatments on $\text{NO}_3\text{-N}$ leaching at different leaching events from (a) Alfisol soil and (b) Spodosol soil.

Figure 5a,b shows the cumulative loss of $\text{NO}_3\text{-N}$ recorded in leachate during the experiment in Alfisol and Spodosol soils, respectively. For Alfisol, cumulative losses of $\text{NO}_3\text{-N}$ were highest with urea and zeo-urea (1:3), but they were statistically similar to those of zeo-urea (1:1) and zeo-urea (1:2). Significantly smaller amounts of $\text{NO}_3\text{-N}$ were leached for the treatments of zeo-urea (2:1) and zeo-urea (3:1), as compared to that from urea (Figure 5a). However, for Spodosol soil, the largest losses of $\text{NO}_3\text{-N}$ were observed for zeo-urea (3:1) and the lowest for zeo-urea (1:1) (Figure 5b). Therefore, zeo-urea (3:1) proved the most effective treatment to reduce leaching of $\text{NH}_4\text{-N}$ for Alfisol soil, whereas less leaching was recorded with zeo-urea (1:1) for Spodosol soils.

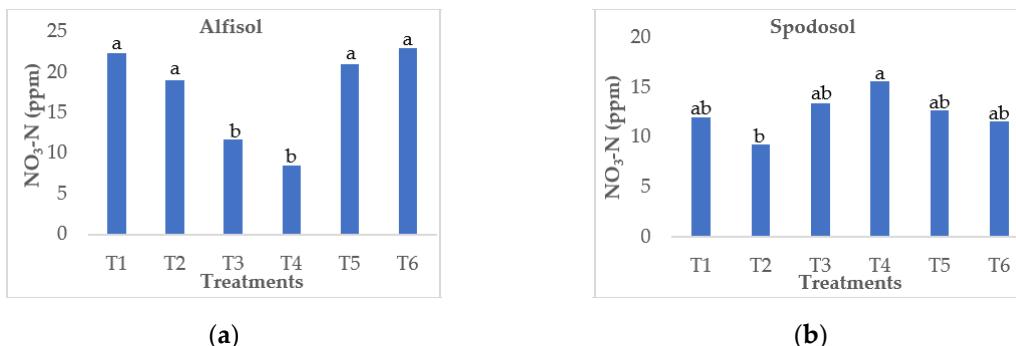


Figure 5. Effect of treatments on cumulative leaching losses of $\text{NO}_3\text{-N}$ from (a) Alfisol soil and (b) Spodosol soil. Means with different letters indicate significant differences among treatments by Tukey's test at $p \leq 0.05$.

3.3. Effect on Ammonia Volatilization Loss

Ammonia volatilization from Alfisol and Spodosol soils is shown in Figure 6a,b. In Alfisol soil, ammonia volatilization was low at days 1, 13, and 20, while increased ammonia volatilization occurred at days 5 and 9 (Figure 6a). Zeolitic urea formulations significantly reduced ammonia volatilization, as compared to that of urea. At day 5, the highest volatilization of ammonia was observed with urea while it was lowest with zeo-urea (1:1) and zeo-urea (1:3). Similarly, at day 9, zeolitic-urea (1:1) resulted in the minimum ammonia volatilization (Figure 6a).

In Spodosol, NH_3 volatilization loss was high at days 1 and 5 and then declined gradually. At day 1, the largest amount of NH_3 was volatilized with urea, but it was statistically similar to zeo-urea (1:2) and zeo-urea (1:3), while ammonia volatilization was lowest with zeo-urea (1:1), zeo-urea (2:1), and zeo-urea (3:1). Zeo-urea (1:1) treatment significantly reduced volatilization loss of NH_3 , as compared to that of the other fertilizer formulations at day 5 (Figure 6b). However, after day 9, NH_3 volatilization was low regardless of treatment.

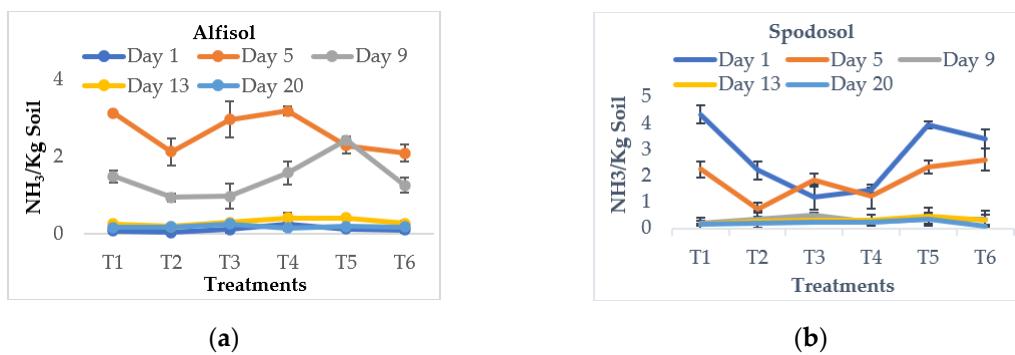


Figure 6. Effect of treatments on NH_3 volatilization at different intervals from (a) Alfisol soil and (b) Spodosol soil.

Figure 7a shows the total amount of $\text{NH}_3\text{-N}$ volatilized from Alfisol soil during the experiment. In Alfisol soil, zeo-urea (1:1) proved to be the most efficient treatment for reducing volatilization loss of $\text{NH}_3\text{-N}$, whereas a larger amount of $\text{NH}_3\text{-N}$ was lost in the other treatments. In Spodosol soil, zeo-urea (1:1) significantly decreased N losses in the form of NH_3 , as compared to that of urea (Figure 7b), but all the treatments of zeo-urea (1:1), zeo-urea (2:1), and zeo-urea (3:1) were statistically similar with respect to ammonia volatilization.

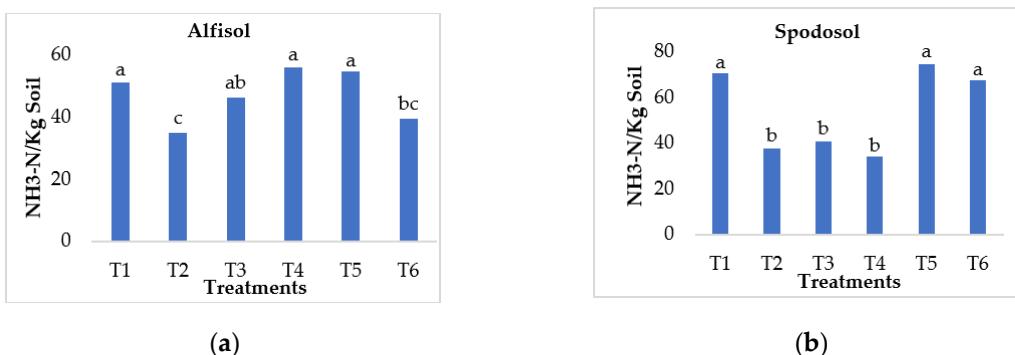


Figure 7. Effect of treatments on cumulative NH_3 volatilization from (a) Alfisol soil and (b) Spodosol soil. Means with different letters indicate significant differences among treatments by Tukey's test at $p \leq 0.05$.

4. Discussion

The surface charges and physio-chemical properties, especially CEC, of zeolites make them a potential binding and adsorbing agent [28]. Zeolites with CEC 119–139 meq/100 g are very effective for the sorption of ammonium [29]. Similarly, hydroxyl functional groups have a great affinity for NH_4^+ . The zeolite used in this study may have sorbed NH_4^+ due to its high CEC (123 meq/100 g). This resulted in a longer retention of ammonium in the soil. However, these results are contradictory to the findings of Iona Rech [30] who reported that zeolites with a CEC of 140 meq/100 g are less effective at retaining NH_4^+ (25 g dm^{-3}) due to competition for sorption by other cations.

Leaching loss of $\text{NH}_4\text{-N}$ was less in soil amended with zeolitic formulations. These results agree with the findings of Swingmann et al. [31] and Colombani et al. [32]. Mahboubeh et al. [33] showed a reduction of $\text{NH}_4\text{-N}$ losses, from 84% to 29%, when soil was treated with $\text{NH}_4\text{-N}$ enriched zeolite. A decrease in total $\text{NO}_3\text{-N}$ leaching was recorded (ranging from 5.9% to 62.3%) with different zeolitic urea formulations, as compared with that of control. A similar effect of zeolite on nitrate leaching was also reported by Omar et al. [34] and Aghaalikhani et al. [35]. They described that the effects of zeolite on nitrate leaching are due to absorption of nitrate into the channels of zeolite. Zeolitic formulations significantly decreased NH_3 volatilization [36–38]. He et al. [39] explained the mechanism for low NH_3 volatilization with zeolite as being due to more $\text{NH}_4\text{-N}$ being retained on zeolite exchange sites.

Further, mixing of zeolite in urea has been reported to decrease N loss. Bernardi et al. [40] recorded that mixing of 25% zeolite in urea resulted in improved fertilizer use by the plants. However, coating of urea with small amounts of zeolite (20%) did not affect N loss in the form of volatilization [41]. A review of the studies involving formulation of zeolitic fertilizers on a weight basis depicted that urea-zeolite fertilizers have been fabricated by using zeolite at 25% and 50% of urea. For example, Dubey et al. [42] developed zeolite coated urea by using 50 g urea with 45 g zeolite powder, which is almost a 1:1 formulation. Mixing of zeolite at the right proportion is of key importance to reduce N losses. Therefore, five zeolite-to-urea ratios were tested for the optimization of zeolite and urea for the reduction of N leaching. Zeo-urea fertilizer at a right proportion can reduce N loss by NH_3 volatilization and $\text{NH}_4^+/\text{NO}_3^-$ leaching due to retention of NH_4^+ on the exchange sites or pores of the zeolite, causing the fertilizer to release more slowly.

A significant decrease in $\text{NH}_4\text{-N}$ loss was noted with zeo-urea (1:1) as compared to that of urea, by 28% and 13 for Spodosol and Alfisol soils, respectively. The greater decrease in $\text{NH}_4\text{-N}$ leaching in the soil treated with zeo-urea (1:1) than that of other formulations may be attributed to the maximum affinity of zeolite for $\text{NH}_4\text{-N}$, on an equal mass basis. In Alfisol, nitrate leaching was significantly decreased by the zeo-urea (2:1) and zeo-urea (3:1). The effect of treatments of zeo-urea (2:1) and zeo-urea (3:1) on $\text{NO}_3\text{-N}$ leaching could be due to the high content of zeolite in the respective formulations or due to the low content of N after excessive loss via NH_3 volatilization and/or $\text{NH}_4\text{-N}$ leaching (Figure 7a).

As depicted by the results, the loss of N in the form of $\text{NH}_4\text{-N}$ was high, especially in Spodosol soil. Clinoptilolite zeolite has the ability to conserve inorganic N in sandy and silt loam soils [43]. Similar results were obtained by Mehrab et al. [44], who reported that $\text{NH}_4\text{-N}$ leaching was higher in light-textured soil and the addition of zeolite significantly reduced $\text{NH}_4\text{-N}$ loss from the amended soil. Up to 84.38% of the applied N in urea and 60.71% in zeo-urea (1:1) were lost in Spodosol soil, as compared to 32.53% in urea and 28.27% in zeo-urea (1:1) in Alfisol soil, indicating that $\text{NH}_4\text{-N}$ leaching loss was higher in light-textured soil (Spodosol) than in Alfisol soil with a higher clay content. This result is in line with the findings of Mahboubeh et al. [33] who estimated $\text{NH}_4\text{-N}$ losses being up to 84% of the applied $\text{NH}_4\text{-N}$ in a sandy soil (sand 92.5%) without zeolite. The cumulative amount of $\text{NH}_4\text{-N}$ in leachate was less from Alfisol soil than from Spodosol, likely due to its higher CEC (Table 1) and subsequently more $\text{NH}_4\text{-N}$ was retained on soil colloidal surfaces. Similarly, interlayers of clay might have held ammonium, resulting in reduced nitrification. Furthermore, higher clay content of soils increases water holding capacity, so this could also be a reason for less leaching loss of $\text{NH}_4\text{-N}$ in Alfisol soil. Clay fixation of $\text{NH}_4\text{-N}$ is high in fine textured soils (90–460 ppm) and medium textured soils (60–270 ppm) as compared with that in coarse textured soils (10–90 ppm), as reported by Nieder et al. and Zhang et al. [45,46].

During the experiment, the concentration of $\text{NO}_3\text{-N}$ in leachate was low in both Alfisol and Spodosol soils. The results were inconsistent with those reported by Malikian et al. [47]. Less aeration could be responsible for this discrepancy. In the present study, the top of each column was covered with a sponge to trap emitted NH_3 , and, thus, it is possible that the nitrification process was affected due to less aeration in the column [48]. Although, the amount of $\text{NO}_3\text{-N}$ in leachate was small in Alfisol soil, no effects of treatments on $\text{NO}_3\text{-N}$ leaching were observed in Spodosol soil. Negatively charged nitrates might have been repelled due to high the CEC of Alfisol and resulted in more leaching of $\text{NO}_3\text{-N}$ from Alfisol as compared with that of Spodosol soil. Furthermore, minimum $\text{NO}_3\text{-N}$ leaching from Spodosol could be due to the high loss of N in the form of $\text{NH}_4\text{-N}$, with a minimal amount being available for nitrification, as evidenced by the double loss of $\text{NH}_4\text{-N}$ in the Spodosol as compared to that of the Alfisol soil (Figure 5a). Volatilization loss of $\text{NH}_3\text{-N}$ accounted for 5.63% and 4% of the total applied N in urea alone, respectively, for Spodosol and Alfisol soils. Maximum NH_3 volatilization occurred at days 5 and 9 in Alfisol but at days 1 and 5 in Spodosol soil. These results are in agreement with Jadon et al. [49]. They

also noticed that volatilization was maximal in the urea-applied soil from days 5 to 10. Less volatilization was recorded in the zeo-urea (1:1) treatment as compared to that of urea alone in both Spodosol soil (46.88%) and Alfisol soil (31.70%). These results are similar to the findings of Sun et al. [50], in which NH_3 volatilization losses were reduced by 35–37% with the addition of zeolite at 10 t per ha.

5. Conclusions

Losses of N in the form of NH_4^+ , NO_3^- and NH_3 were reduced in the soils amended with zeolitic formulations, as compared with that of the urea fertilizer. Zeo-urea (1:1) significantly reduced leaching of $\text{NH}_4\text{-N}$ and NH_3 volatilization in both Alfisol and Spodosol soils. Nitrate release into the leachate was also delayed by zeo-urea (1:1) in Alfisol, while in Spodosol soil none of the zeolitic formulations significantly affected nitrate leaching. These results indicate that in the present study, zeo-urea (1:1) was the most effective fertilizer formulation for reducing N losses from applied urea, especially in Alfisol soil.

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