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Nitrogen Recovery Efficiency from Urea Treated with NSN Co-Polymer Applied to No-Till Corn

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Abstract: Nitrogen (N) rate increases used by many farmers produce a reduced or null effect on N recovery efficiency (RE) by crops. Therefore, management practices to reduce N losses and increase RE are necessary. Co-polymer maleic itaconic acid (NSN) have become available for use with urea and has shown potential in reducing N losses. The objective of this study was to evaluate the effectiveness of urea treated with NSN on grain yield and RE in a no-till corn. A field experiment was carried out at Balcarce, Argentina over three years, evaluated treatments were urea and urea + NSN at 120 N kg ha^{-1}, and additional 0 N treatment was included. Urea + NSN was effective to reduce total ammonia volatilization losses, and the average of two years were 1.4 (1.1% to N applied) and 8.7 kg ha^{-1} (7.2% to N applied) for urea + NSN and urea, respectively. However, while grain yield and N grain removal were not affected by urea + NSN, the N rate significantly increased grain yield and N grain removal. Nitrogen recovery efficiency was not affected by urea + NSN, RE (average of three years) was 29.0% and 27.8% for urea and urea + NSN, respectively. In conclusion, there was no advantage of using urea treated with NSN in no-till corn overgrain yield, N grain removal, or RE.

Keywords: *Zea mays* L.; nitrogen fertilization; N grain removal

1. Introduction

Nitrogen (N) is often the most yield-limiting nutrient, particularly in corn (*Zea mays* L.) production systems [1]. Agriculture intensification and use of crops with higher grain yield potential have increased N fertilizer rates, with a reduced or null effect on the improvement in N recovery efficiency (RE) by the crops [2]. Efficient use of N in crop production is crucial for increasing crop yield and quality, environmental safety, and economic considerations [3,4]. Therefore, it is necessary to develop fertilization management strategies that maximize fertilizer N recovery through decreasing N losses.

Urea (46% N) is the most commonly used N fertilizer in Argentina and is generally surface-broadcast applied. Broadcasting fertilizers that produce NH_4^+ (urea and UAN) could result in large ammonia volatilization losses (NH_3-N). The magnitude of NH_3-N losses in no-till scenarios is affected by environmental factors (humidity, temperature, and wind), soil (pH, buffer capacity, cation exchange capacity, organic matter), crop (quantity and type of crop residues), N source and rate [5–7], and fertilization time and placement [8–11].

Globally, up to 64% of applied N is lost as NH_3-N, therefore, NH_3-N volatilization is a major pathway of N loss in agricultural systems worldwide and, consequently, produce low fertilizer N use efficiency [12]. The use of non-urea-based fertilizers reduce fertilizer application rates, and deep placement of fertilizers, irrigation, urease inhibitors, and controlled release fertilizers are effective in reducing NH_3-N volatilization. Among the enhanced efficiency fertilizers, urease inhibitors and controlled release fertilizers decreased NH_3-N volatilization by 54% and 68%, respectively whereas nitrification inhibitors increased NH_3-N volatilization by 38%. These results confirm that N loss can be mitigated through the adaption of appropriate fertilizer products [12].

Co-polymer maleic and itaconic acids (Nutrisphere-N, or NSN) are a 30–60% co-polymer of maleic and itaconic acid that, according to the product literature, inhibits nitrification through complexing soil copper ions and inhibits urease activity by complexing nickel ions within the urease enzyme itself [13,14]. NSN has become available for use with urea-containing fertilizers and has shown potential in reducing N losses [15,16]. The material is reported to have the ability to slow urea hydrolysis and the nitrification process through effects on metalloenzymes, such as urease and the soil N oxidation enzymes of *Nitrosonomas* and *Nitrobacter*. Each of these enzyme's action depends on a specific multivalent metallic co-factor, respectively nickel, copper, and iron [17,18]. The polymer, NSN, is theorized to sequester or compromise the activities of these metals with a resulting slowing of the respective reactions [19]. NSN polymer coating reduces urea hydrolysis, thereby reducing NH_3-N volatilization and increasing the agronomic efficiency of urea-based N fertilizers [16,19]. However, published studies demonstrating that NSN inhibits soil urease have not been found. Adding NSN to urea had little effect on urease activity or ammonia volatilization [20]. Currently there is little information on the relative effectiveness of these materials in a field environment. The objective of this study was to evaluate the use of urea treated with NSN on grain yield and recovery efficiency (RE) in a no-till corn.

2. Materials and Methods

The experiment was conducted for three years over long-term cropped soil, at Balcarce, Argentina (130 m above sea level; 870 mm mean annual rainfall; 13.7 °C mean annual temperature), on a soil complex of a fine, mixed, thermic Typic Argiudoll with less than a 2% slope. The soil has a loam texture at the surface layer (0–0.20 m depth), with an average particle size distribution of 23% clay, 36% silt, and 41% sand. The subsurface layer (0.25–1.10 m depth) has a clay-loam texture. Surface horizon characteristics (0–0.2 m) at the beginning of the experiment are presented in Table 1.

The experimental area was under NT (more than seven years), in all years preceding crop was wheat (*Triticum aestivum* L.) and, ground cover by residues ranged from 80% to 90%. The experimental design was a randomized complete block with three replications and two combinations of Urea (with and without Nutrisphere-N) at a 120 kg ha^{-1} N rate plus a control treatment (0 N). Urea fertilization was applied broadcast on the surface at planting time in years 1 and 3, and at the six leaf phenological stage (V6) [21] in year 2. NSN polymer was added evenly sprayed (impregnated) onto the urea at a rate of 0.25% (1/2 gallon of NSN per ton of urea) immediately before application.

Table 1. Soil characteristics during planting of maize for three growing seasons at Balcarce, Argentina.

Growing Season	P †	N-NO_3^-	pH	OM ‡
	(0–20 cm) mg kg^{-1}	(0–60 cm) kg ha^{-1}		(0–20 cm) %
Year 1	19.5	42.0	5.6	4.9
Year 2	15.0	39.8	5.7	5.4
Year 3	8.2	74.4	5.9	5.1

P † = Phosphorus Bray I [22], OM ‡ = Organic Matter [23].

In all years, individual plots were five rows wide (0.52 m) and 12 m long (31.2 m^2). Weeds and insects were chemically controlled with recommended products and rates. Plots were fertilized at planting with 20 kg P ha^{-1} as triple superphosphate (0-46-0), and 15 kg S ha^{-1} as calcium sulfate (18.6% S). The crop was irrigated during first two years as needed so those production factors did not limit crop growth. Crop evapotranspiration (CET) was determined as the product between potential evapotranspiration (ETO) and crop coefficient (Kc) [24]. The ETO was determined according to Pennman (1948) [25]. The crop coefficients (CET/ETO) are those reported for the area by Della Maggiora et al. (2002) [26].

Ammonia volatilization losses were evaluated in the first two years. A semi-open static system [27] was used to monitor NH_3-N volatilization losses from the plots. It consisted of one polyvinyl chloride cylinder (30 cm diameter, 50 cm height) per experimental unit, containing two polyurethane sponges 12 cm apart saturated with 0.5 M sulfuric acid (H_2SO_4). The lower sponge was placed 30 cm above the soil surface and was used to capture the NH_3-N volatilized from soil. The second sponge was placed 4 cm below the top of the cylinder to prevent NH_3-N from the atmosphere from entering the chamber and contaminating the lower sponge. The sponges were changed every 24 or 48 h and washed with 1.5 L of deionized water. An aliquot of 25 mL was alkalinized with 40% sodium hydroxide (NaOH) and NH_3-N was determined by microdistillation [28]. Measurements of NH_3-N volatilization were started at the time of fertilizer application and continued either until the losses from fertilized treatments were negligible and equaled those from 0 N treatment, or until a total of 10 mm of rain fell. The occurrence of rainfall events (>10 mm) interrupted the volatilization process [29]. Immediately after every rainfall event the chamber was moved in the same plot to ensure that the measured period reflected the environmental conditions (rain, wind, temperature) of the previous period.

At physiological maturity, three 7.15-m-long interior rows (11.15 m^2) of each experimental unit were hand-harvested to determine grain yield. Grains were oven dry weighed, and milled to pass a 1-mm mesh. Total N in grain was determined by the Dumas method using a LECO TruSpec analyzer (LECO CORPORATION, St Joseph, MI, USA) [30]. Nitrogen grain removal was calculated as the product of N concentration and dry weight. Grain yields were corrected to a 140 g kg^{-1} grain moisture content.

Nitrogen recovery efficiency in grain (%RE) was calculated as:

$$RE = (GNF - GNT)/N\ rate \times 100 \quad (1)$$

where GNF and GNT are grain N content in the fertilized treatment and grain N content in the 0 N treatment, respectively.

Analysis of variance was carried out using the SAS 9.1 software [31]. Treatment means were compared using the LSD mean separation procedure (5%).

3. Results and Discussion

3.1. Climatic Conditions

The water balances for corn crops during the growing seasons are presented in Figure 1. In year 1, where the rainfall registered from October to March plus irrigation totaled 450 mm, a light water deficit event was registered at the beginning of critical kernel set period [32]. This water stress (60 mm) would lightly affect corn grain yield (Figure 1). On the other hand, during corn growing seasons in years 2 and 3 a pronounced stress took place during January (92 mm and 122 mm of water deficit in years 1 and 2, respectively) (Figure 1), a period in which water availability is crucial for obtaining high corn yields [33]. Thus, corn grain yield may have been affected by water availability.

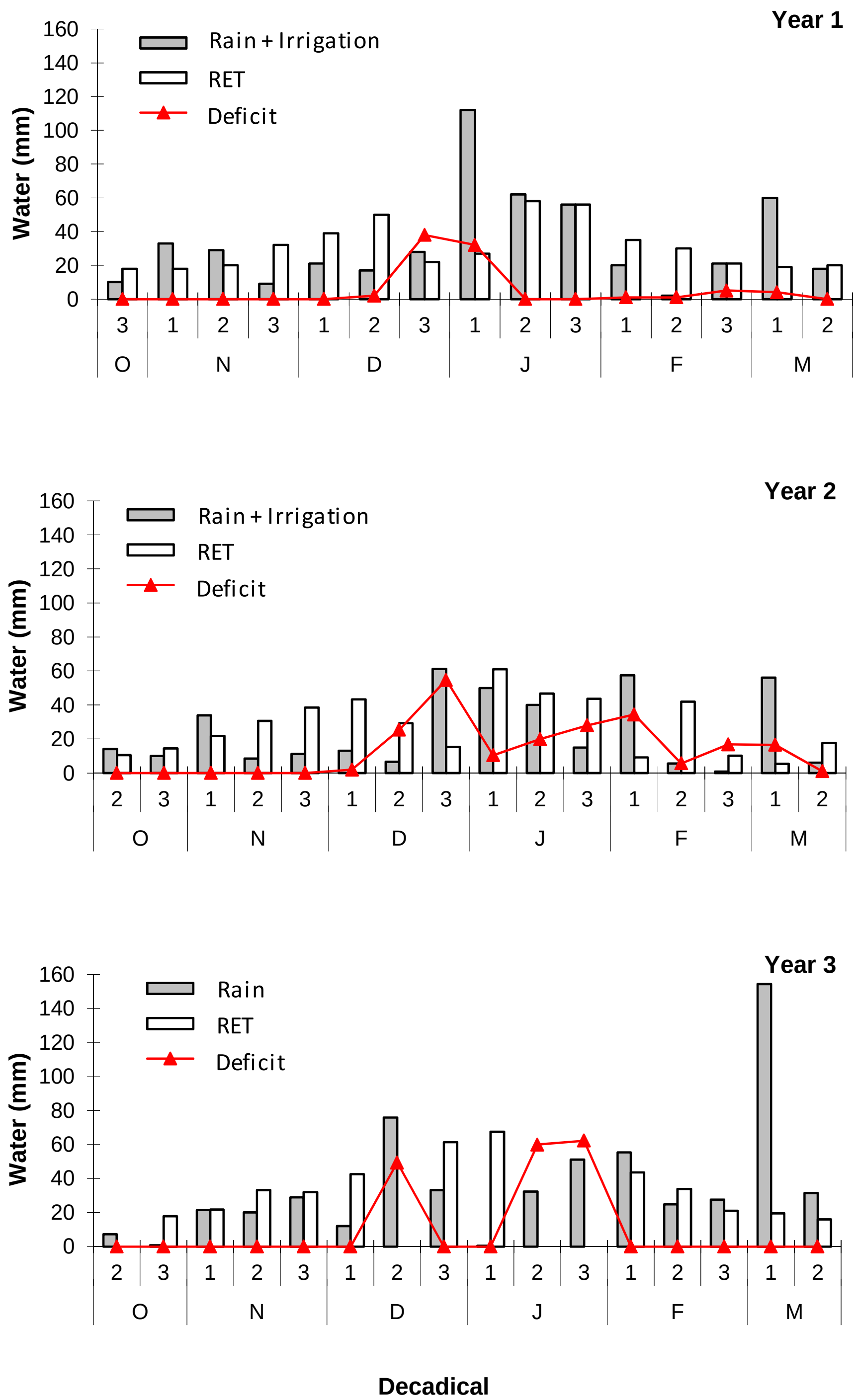

Figure 1. Precipitation, real evapotranspiration (RET), and water deficit during three years on no-till corn.

3.2. Ammonia Volatilization Losses

Ammonia volatilization losses were during a period of seven and 18 days in Years 1 and 2, respectively (Figure 2). In Year 1, NH_3-N volatilization losses from urea was significantly higher than urea + NSN during all experimental periods (seven days), while NH_3-N volatilization losses from urea + NSN were not different from 0 N treatment (Figure 2). Total NH_3-N volatilization losses were 13.1 (11.0% of applied N) and 0.5 kg ha^{-1} (0.4% of applied N) from urea and Urea + NSN, respectively (Figure 3). In year 2, a lack of precipitation produced a low rate of urea hydrolysis until three days after fertilization, after that 13 mm precipitation incorporated N into the soil profile and, therefore, NH_3-N volatilization losses were low [29] (Figure 2). In general, NH_3-N volatilization losses from urea were significantly higher than urea + NSN from days 1–8. Fertilization treatments were different to 0 N treatment from day 9–18 (Figure 2). Total NH_3-N volatilization losses determined were 4.5 (3.8% of applied N) and 2.5 kg ha^{-1} (2.1% of applied N) from urea and urea + NSN, respectively (Figure 3). In both years, higher rates of NH_3-N volatilization losses were observed during a third day after fertilization as a consequence of higher soil pH values [34] due to the high alkalinity induced by the urea hydrolysis. Ammonia volatilization losses form urea treatment were similar to those reported in the area [9,10,35,36], and lower than losses reported by other authors [29,37]. This difference could be attributed to the slightly acid pH of the soil under study (Table 1) and to higher titratable acidity due to its high soil organic matter content [38] (Table 1). Higher levels of titratable acidity reduce volatilization losses because of the greater soil buffer capacity [34]. These results showed that NSN was effective in reducing NH_3-N volatilization losses. Similar results were informed by Pereira et al. (2009) [15] and Gordon (2014) [16]. However, Franzen et al. (2011) [20], Goos (2013) [39], and Chien et al. (2014) [40] reported that NSN had the weakest or null effect on reducing ammonia losses.

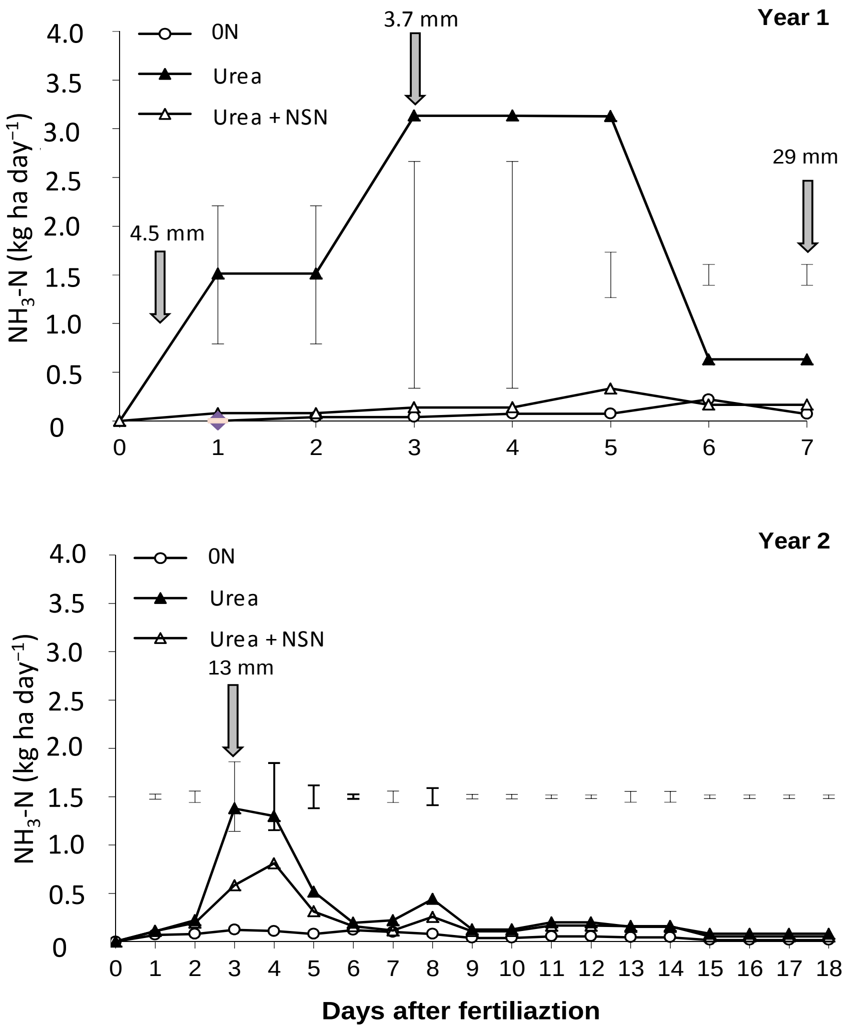

Figure 2. Rates of ammonia N volatilization losses (NH_3-N, kg ha day^{-1}) from urea or urea treated with NSN (urea + NSN) applied broadcast on the surface to no-till corn during two years. Arrows indicate rainfall dates and amount. Vertical bars indicate LSD test (0.05) values. NSN, maleic itaconic acids.

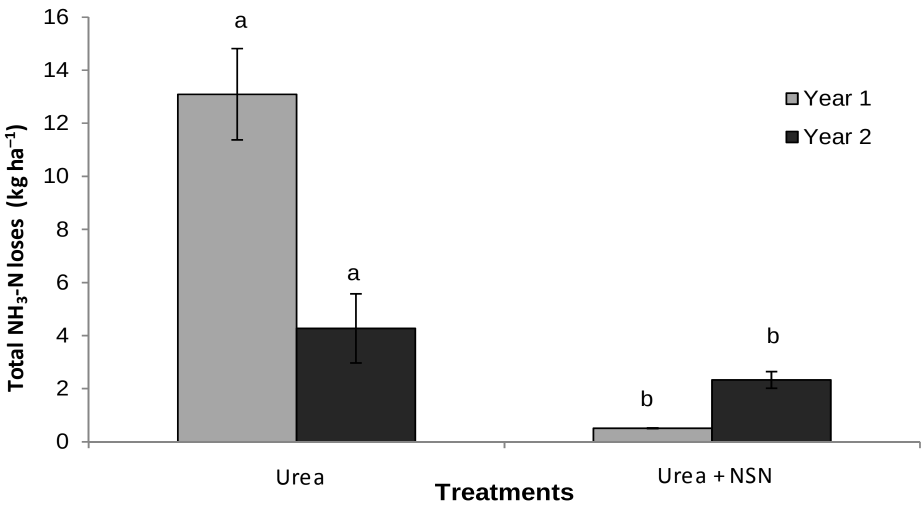

Figure 3. Total N loses from urea and urea treated with NSN (urea + NSN) applied broadcast on the surface to no till corn during two years. Within the years, means followed by the same letter are not significantly different from each other based on the LSD test (0.05). Vertical bars indicate standard error. NSN, maleic itaconic acid.

3.3. Grain Yield, N Grain Removal, and Recovery Efficiency

Over three years, corn grain yield was not significantly increased by the use of NSN (Figure 4). A similar result was informed by Pereira et al. (2009) [15]. Grain yield was significantly increased by N fertilization (Figure 4). Averaging of the three years, the N response was 1040 kg ha^{-1}. No yield increases in the use of NSN was the consequence of the NH_3-N volatilization losses from urea were not very high (Figure 3). High grain yield was determined in control treatments and, therefore, a low response to applied N could be a consequence of high N mineralization from organic matter and soil N content at planting time (Table 1). The soils of the area contain relatively high levels of organic matter (Table 1), therefore, the amount of N mineralized from the soil organic fraction during the crop growing season would be important [41]. Under adequate water availability conditions, N supplied by mineralization during the maize growing season can vary from 100 to 250 kg N ha^{-1}, depending on soil management practices (years from last pasture, crop rotations, etc.) [42].

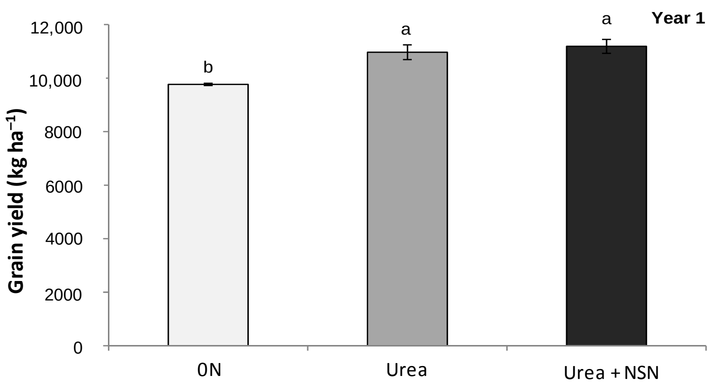

Figure 4. *Cont.*

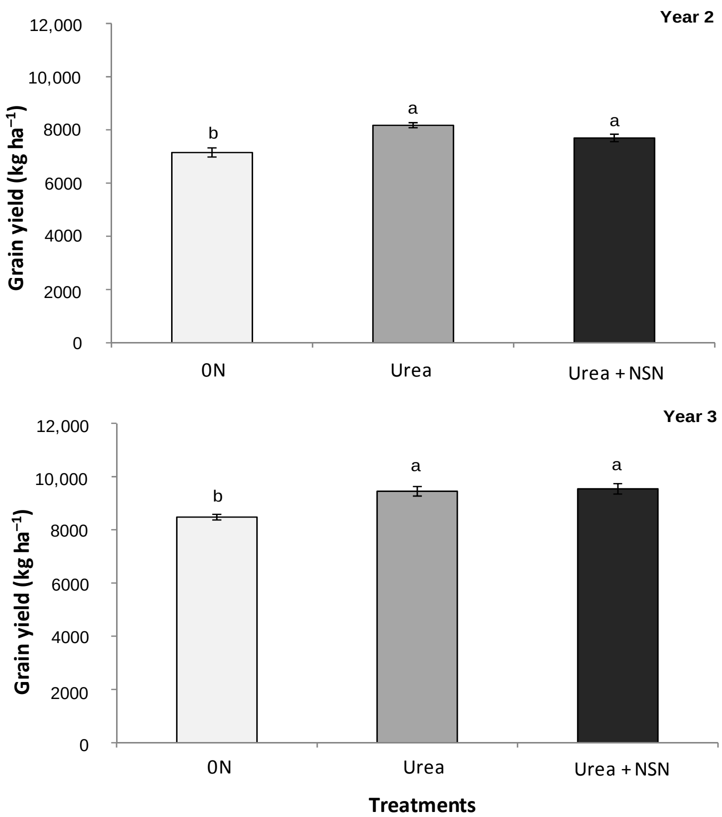

Figure 4. Grain yield affected by N rate and urea or urea treated with NSN (urea + NSN) applied broadcast on the surface to no-till corn during three growing seasons. Means followed by the same letter are not significantly different from each other based on the LSD test (0.05). Vertical bars indicate standard error. NSN, maleic itaconic acid.

Nitrogen grain removal was not significantly affected by the use of NSN, and similar to the observed grain yield, only a significant N response was determined (Figure 5). No response in grain yield and N grain removal using NSN were reported by Franzen et al. (2011) [20] on spring (*Triticum aestivum* L.) or durum [*Triticum turgidum* L. subsp duram (Desf.) Husn.] wheat in North Dakota, and rice (*Oriza sativa* L.) in Mississippi and Arkansas. However, Gordon (2014) [16] showed significant corn (*Zea mays* L.) grain yield and grain N concentration by using NSN. Similar results were found by Wiatrak and Gordon (2014) [43] in corn with fall N applications.

Over three years, RE was not significantly increased by the use of NSN (Figure 6). No significant differences were seen in grain yield and grain N content between urea and urea + NSN (Figures 4 and 5), and consequently produce a similar RE by use of NSN (Figure 6). Averaged across years, RE was 29% and 28% for urea and urea + NSN, respectively. The RE values determined in the experiments was inferior to information by Sainz Rozas et al. (2004) [9] for the area (45–55%). Low RE determined over three years could be a consequence of a greater N mineralization from organic matter [42], N losses by denitrification [44], or immobilization [9]. On the other hand, NO_3-N leaching would be important in the operation of NT maize cropping systems in the area [9]. NSN was ineffective in increasing N efficiency for corn (*Zea mays* L.), winter wheat (*Triticum aestivum* L.) [45], and sugarbeet (*Beta vulgaris* L.) [46].

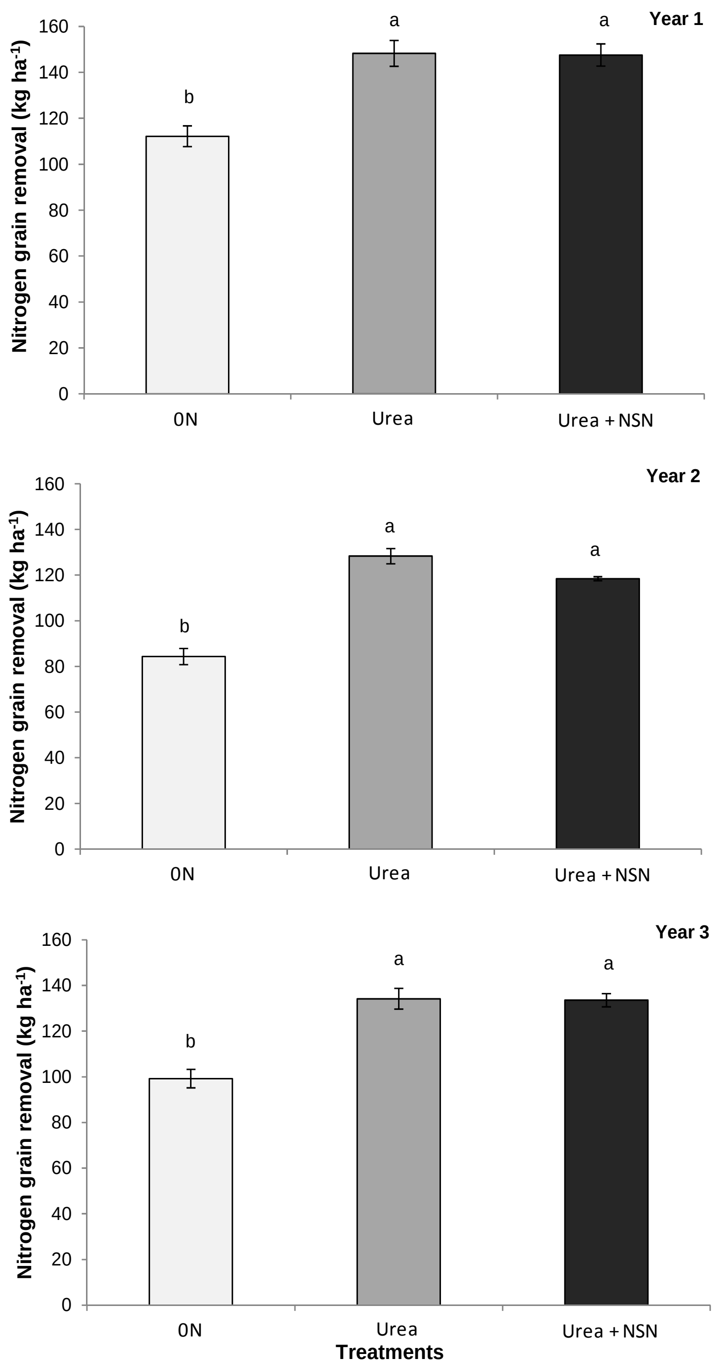

Figure 5. Nitrogen grain removal affected by the N rate and urea or urea treated with NSN (urea + NSN) applied broadcast on the surface during three growing seasons to no-till corn. Means followed by the same letter are not significantly different from each other based on the LSD test (0.05). Vertical bars indicate standard error. NSN, maleic itaconic acid.

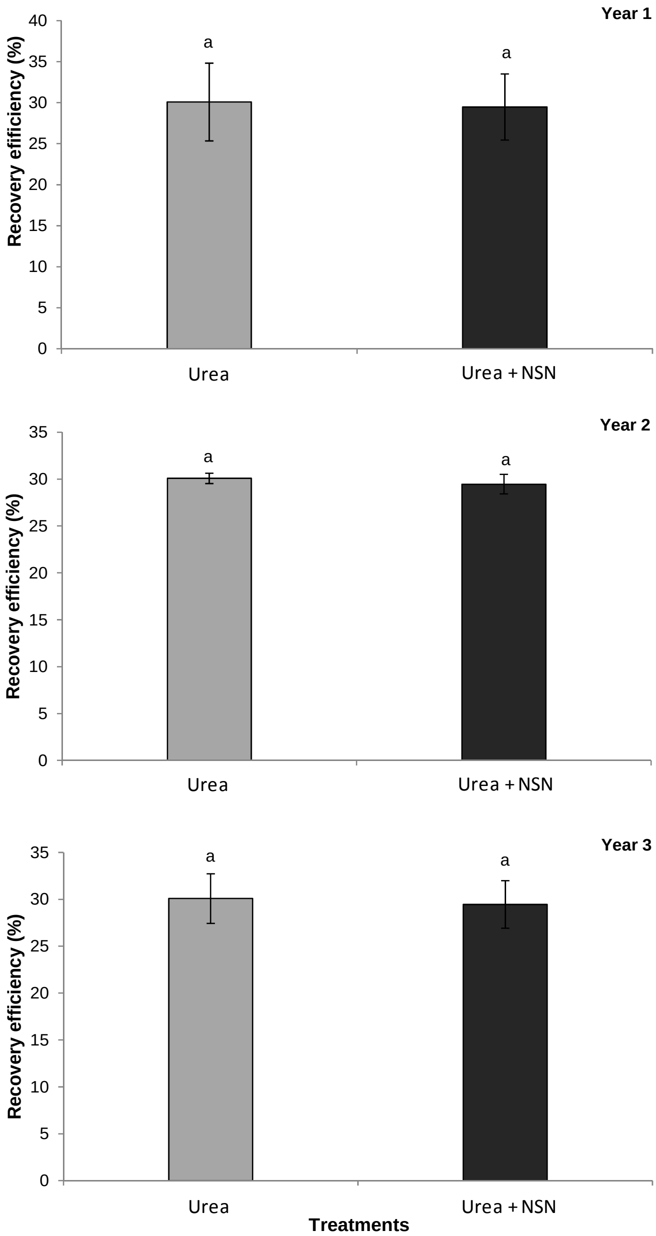

Figure 6. Nitrogen recovery efficiency (RE) affected by urea or urea treated with NSN (urea + NSN) applied broadcast on the surface during three growing seasons to no-till corn. Means followed by the same letter are not significantly different from each other based on the LSD test (0.05). Vertical bars indicate standard error. NSN, maleic itaconic acid.

4. Conclusions

Urea treated with NSN was effective to reduce total ammonia volatilization losses in no-till corn. However, the results from three-year experiments show no advantage in grain yield, N grain removal, or RE with the use of urea treated with NSN.

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