

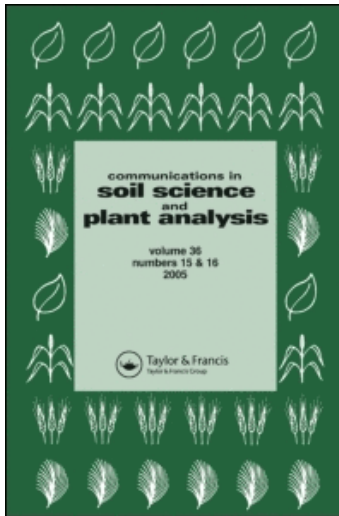
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AMMONIUM FIXATION FROM UREA AS INFLUENCED BY NITRAPYRIN

KEY WORDS: Nitrogen fixation, Nitrification inhibitors

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ABSTRACT

During the period 1977-1979,  $\text{NaNO}_3$ , urea, and urea plus 2% (wt/wt) nitrapyrin (2-chloro-6-(trimethyl)pyridine) were compared on a Matapeake silt loam (fine silty mixed mesic Typic Hapludult). Nitrogen sources were injected as solutions into the water system at  $224 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  used for subsurface trickle irrigation of corn (*Zea mays* L.). Nitrogen was withheld in 1980 in order to assess residual N effects. Grain yields in 1980 for the  $\text{NaNO}_3$ , urea, and urea plus Nitrapyrin treatments were 5.10, 4.56 and 6.52  $\text{Mg ha}^{-1}$ , respectively. Corresponding ear leaf N concentrations were 17.7, 16.7 and 19.2  $\text{g kg}^{-1}$ . Significantly higher grain yield and leaf N concentrations associated with the use of nitrapyrin as a nitrification inhibitor indicated greater soil N reserves for this treatment. Non-exchangeable (fixed)  $\text{NH}_4^+$  in soil cores taken in November 1981 averaged 54, 59 and 74  $\text{ug N g}^{-1}$  for the respective N regimes. The concentration of fixed  $\text{NH}_4^+$  increased

with sampling depth, averaging 54, 61 and 72  $\mu\text{g N g}^{-1}$  for the 0-5, 30-35, and 60-65 cm profile depths, respectively. This trend is ascribed to increasing quantities of micaceous and vermiculitic clay (<2  $\mu\text{m}$ ) with increasing profile depth.

### INTRODUCTION

In coarse textured Coastal Plain soils, N is readily lost via leaching and denitrification due to low clay and organic matter contents. Apart from wasting expensive fertilizer,  $\text{NO}_3$  leaching may contribute to ground water pollution. Increased N efficiency in these soils is therefore exceedingly important, both for the farmer and for the environment.

Considerable promise for improving the efficiency of N fertilizer use has been afforded by the advent of nitrification inhibitors such as Nitrapyrin (2-chloro-6(trichloromethyl)-pyridine) (1). When Nitrapyrin is applied with  $\text{NH}_4^+$  fertilizer it delays the conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  by inhibiting the activity of Nitrosomonas. This reduces the amount of N losses due to volatilization and leaching (2).

Numerous studies have shown that Nitrapyrin increases yields of crops (3, 4, 5, 6). Regardless of the crop grown or the mode of application of the inhibitor, Nitrapyrin will not increase yields at recommended levels of N fertilization unless excessive  $\text{NO}_3^-$  losses occur through leaching or denitrification (4).

It has been known for sometime that many soils have the ability to fix and hold substantial amounts of added  $\text{NH}_4\text{-N}$  and that some soils contain large quantities of indigenous fixed  $\text{NH}_4^+$  and also have the ability to release this N in an available form for crop use (7, 8). The amount of fixed  $\text{NH}_4^+$  (nonexchangeable  $\text{NH}_4^+$ ) present in soil depends to a large extent on the kind and amount of layer silicate minerals present. The soil minerals that are chiefly responsible for  $\text{NH}_4$  fixation are vermiculite and soil mica (9, 10). Vermiculite has been shown to have the greatest capacity to fix  $\text{NH}_4^+$ . To date, no reports have appeared in the scientific literature on the effects of Nitrapyrin on  $\text{NH}_4^+$  fixation.

The purposes of this study were: (1) to investigate the residual effects of various N treatments and Nitrapyrin on corn yield on a Delaware soil and, (2) to investigate the influence of Nitrapyrin on  $\text{NH}_4\text{-N}$  fixation in soils.

## MATERIALS AND METHODS

### Field Studies

During the period 1977-1979, three N regimes were established in a randomized complete block design with three replications on a Matapeake silt loam (fine silty mesic Typic Hapludult) at the University of Delaware Research Farm in Newark, Delaware. Nitrogen sources for the respective regimes were  $\text{NaNO}_3$ , urea, and urea plus 2% Nitrapyrin (2-chloro-6 (trichloromethyl) pyridine). Nitrogen sources were injected as solutions into a subsurface irrigation system at  $224 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . Residual N effects were assessed by corn (*Zea mays* L.) yields and by the amount of nonexchangeable  $\text{NH}_4\text{-N}$  in 1981.

### Laboratory Analyses

Bulk soil samples were taken in November 1981 from the 0-5, 30-35 and 60-65 cm depths of each plot. Soil samples were air dried and crushed to pass a 2-mm sieve in preparation for laboratory analyses.

Particle size analyses were determined on each sample using the pipet method (11) and organic matter was determined using the modified Walkley-Black procedure (12). The mineralogy of the <2  $\mu\text{m}$  clay fraction was determined by X-ray diffraction using methods outlined by Sparks and Rehcigl (13). Data for these analyses are given in Table 1.

Nonexchangeable  $\text{NH}_4^+$  was measured by extracting with alkaline  $\text{KOH-Cl}$  to selectively remove exchangeable  $\text{NH}_4\text{-N}$  associated with clay and organic colloids. The samples were then extracted with a 5 M HF-1 M HCl solution to promote release of fixed  $\text{NH}_4\text{-N}$  (14). The  $\text{NH}_4^+$  was then determined by steam distillation. All data were evaluated statistically using linear regression analyses (15).

TABLE 1

Selected Chemical, Mineralogical, and Physical Properties of a Matapeake Silt Loam.

Horizon	<u>Particle Size Analysis</u>			Organic Matter	Mineral suite of
	Sand	Silt	Clay		< 2 um clay fraction
	-----g kg <sup>-1</sup> -----				
Ap	145	700	155	19	VR <sub>1</sub> , VC <sub>2</sub> , MI <sub>3</sub> , QZ <sub>4</sub>
B <sub>2</sub> h	70	750	180	6	VC <sub>1</sub> , VR <sub>2</sub> , MI <sub>3</sub> , QZ <sub>4</sub>

VC = Chloritized vermiculite, VR = Vermiculite, MI = Mica, QZ = Quartz.

Subscript 1 = most abundant; 4 = least abundant.

### RESULTS AND DISCUSSION

Corn yields in 1980 were significantly greater on plots that had previously received urea plus Nitrapyrin compared to plots having received either urea or NaNO<sub>3</sub> (Fig. 1) being 6.5, 4.5 and 5.1 Mg ha<sup>-1</sup> for the urea + Nitrapyrin, urea, and NaNO<sub>3</sub> treatments, respectively. Ear leaf N concentrations were also significantly greater for the urea plus Nitrapyrin treatment with levels of 19.2, 16.7 and 17.7 g kg<sup>-1</sup>, in the urea + nitrapyrin, urea, and NaNO<sub>3</sub> treatments, respectively. In addition, there was a strong correlation between leaf N levels and corn yields (Fig. 2). The greater yields and leaf N concentrations observed in plots that received urea plus Nitrapyrin indicates greater soil N reserves in this regime.

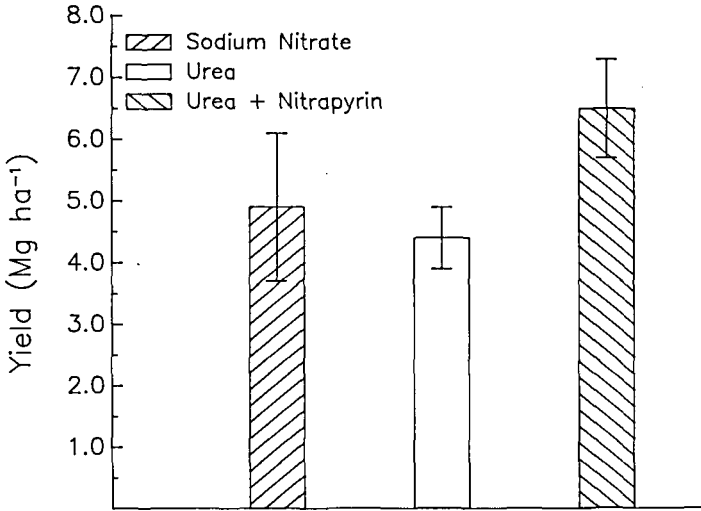


Figure 1 Corn grain yields as influenced by  $\text{NaNO}_3$ , urea and urea plus Nitrapyrin on a Matapeake silt loam.

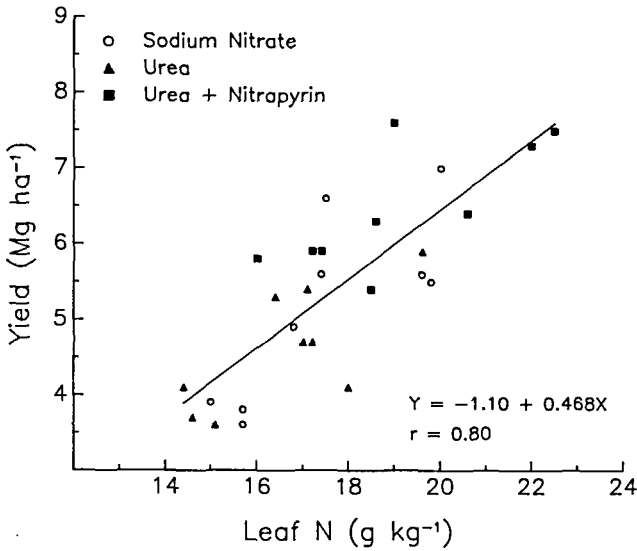


Figure 2 Corn grain yields as influenced by leaf N levels and N source on a Matapeake silt loam.

It was hypothesized that Nitrapyrin might increase  $\text{NH}_4^+$  fixation by the 2:1 vermiculitic and micaceous clay minerals present in the Matapeake soil (Table 1) by effectively suppressing the conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ . Since N was withheld in 1980, the diffusion gradient could favor the release of this fixed  $\text{NH}_4^+$  and thereby account for at least a portion of the yield increase associated with Nitrapyrin. Accordingly, we investigated the hypothesis that yield and tissue concentrations were increased on the urea plus Nitrapyrin plots due to enhanced  $\text{NH}_4^+$  fixation.

As Fig. 3 shows, the urea plus Nitrapyrin treatment fixed significantly more  $\text{NH}_4^+$  than the urea or  $\text{NaNO}_3$  treatments, regardless of soil depth. The amount of fixed  $\text{NH}_4^+$  was clearly a function of percent clay present (Fig. 4). This has been substantiated by other investigators (7, 16). Within each N regime, fixed  $\text{NH}_4^+$  increased with sampling depth averaging 54, 61 and 72  $\mu\text{g N g}^{-1}$  for the 0-5, 30-35 and 60-65 Cm profile depths, respectively (Fig. 3). This trend was attributed to higher quantities of clay with increasing depth (Table 1). The clay was predominantly micaceous and vermiculitic which are known to be N fixing minerals (7). It should be noted (Fig. 4) that the slopes are similar for the urea plus Nitrapyrin and the urea treatments further suggesting that Nitrapyrin increases  $\text{NH}_4^+$  fixation by inhibition of nitrification.

It is now generally accepted that some form of dynamic equilibrium exists between fixed and exchangeable  $\text{NH}_4^+$ . Accordingly,  $\text{NH}_4^+$  fixation occurs when the concentration of exchangeable  $\text{NH}_4^+$  exceeds the equilibrium value. Fixed  $\text{NH}_4^+$  is released when the exchangeable  $\text{NH}_4^+$  drops below this equilibrium value and consequently the fixed  $\text{NH}_4^+$  may gradually be liberated from soils and clay minerals if the  $\text{NH}_4^+$  released is removed from the system (17).

The results of this study show that where clay minerals such as micas and vermiculites are present in soils and Nitrapyrin is applied as a nitrification inhibitor, considerable N may be

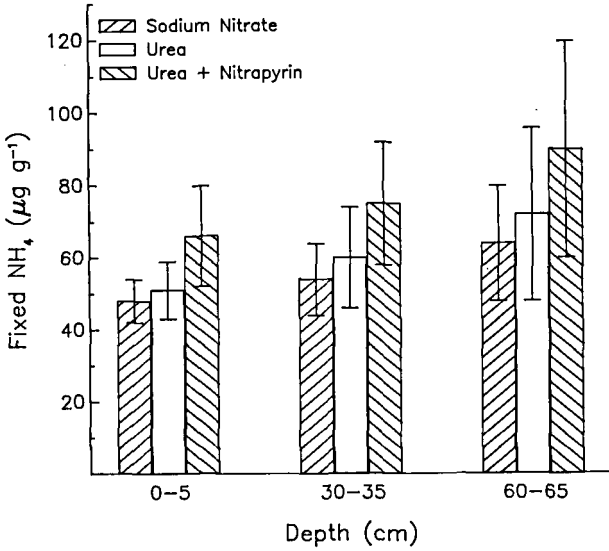


Figure 3 Fixed  $\text{NH}_4^+$  as influenced by  $\text{NaNO}_3$ , urea, and urea plus Nitrapyrin treatments and sample depth in a Matapeake silt loam.

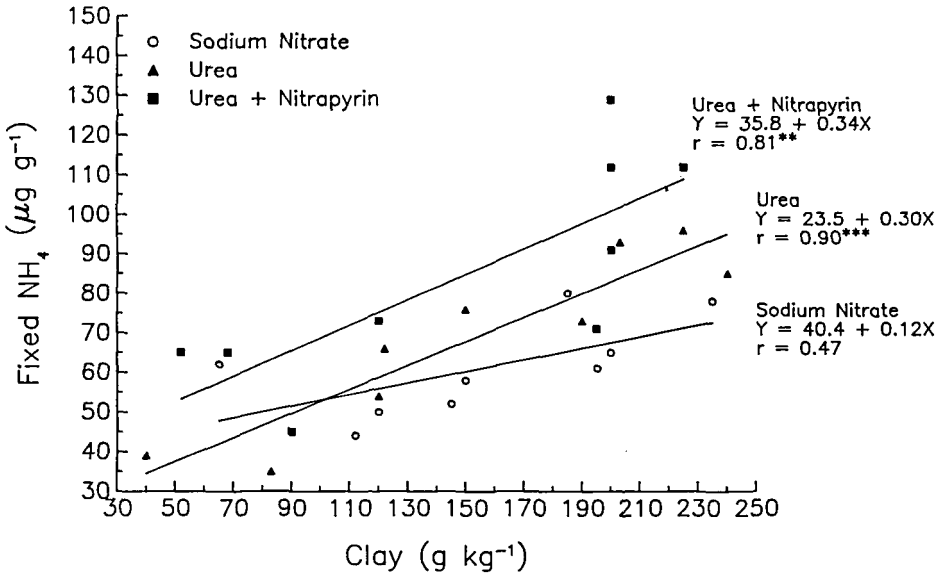


Figure 4 Fixed  $\text{NH}_4^+$  as influenced by  $\text{NaNO}_3$ , urea, and urea plus Nitrapyrin treatments and concentrations of soil clay in a Matapeake silt loam.

converted to nonexchangeable forms. This can become an important source of N for crops at a later date and can cut down on the fertilizer requirements.

#### ACKNOWLEDGEMENTS

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