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Effect of the nitrification inhibitors 1-amidino-2-thiourea and dicyandiamide in combination with urea and ammonium sulfate

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Abstract

The efficiency of the nitrification inhibitors dicyandiamide (DCD) and 1-amidino-2-thiourea (or guanylthiourea = GTU) in reducing losses from N fertilizers was investigated in two greenhouse experiments where leaching of nitrate-N was induced by percolation at 3 and 5 weeks after fertilization.

At an application rate of 10% by weight of fertilizer-N (e.g. 10 kg GTU/ha), GTU in combination with ammonium sulfate (AS) had effects similar to those of DCD (e.g. 15 kg DCD/ha) with regard to nitrate leaching, plant yields and nitrogen uptake. However, in combination with urea (U), GTU was more effective than DCD when applied at the same ratio except with a humic sandy clay soil (pH 7.3, 4.4% organic C), where GTU did not perform as effectively. Nitrate leaching was reduced by as much as 50% using U/GTU instead of U/DCD, and plant yield increased by 30%.

At temperatures between 17 and 25°C, the combination U/GTU could protect a high percentage of the nitrogen from being nitrified and leached over a 3 to 5 weeks period. The superiority of GTU over DCD was demonstrated especially in the treatments with 5 weeks of preincubation, despite the considerably lower application rate.

Introduction

Nitrification inhibitors selectively retard the bacterial transformation of NH_4^+ to NO_3^-; nitrogen is maintained for an extended period in the NH_4-form and nitrate is released after some months or weeks, depending on temperature. By adding nitrification inhibitors, ammonium fertilizers or urea can be maintained in the ammonium form, producing higher efficiencies than conventional N fertilizers under site conditions which admit high nitrogen losses by leaching or denitrification. A large amount of research has been done on the nitrification inhibitor dicyandiamide (DCD) [1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 12, 13, 14, 15].

In previous studies [7, 8] it was pointed out that 1-amidino-2-thiourea (or guanylthiourea = GTU), especially in combination with urea (U), offers a promising possibility to make N fertilizers more efficient. It has the same advantages as DCD over other nitrification inhibitors:

- its breakdown is known [2, 3, 5, 11],
- no toxic effects on other soil organisms, plants or higher organisms have been observed,
- it can be combined with solid fertilizers since it is non-volatile,
- at an estimated price of 9 DM/kg GTU, its application rate is agronomically economical.

Other information concerning GTU and its reactions are:

- it is decomposed in soil via 3,5-diamino-1,2,4-thiadiazole (TDZ) to DCD (Fig. 1) [7, 8, 16],
- each of these compounds shows nitrification inhibition [7, 8],
- it can be taken up by plants where it is also degraded via TDZ to DCD [7, 16].

The degradation in soils is influenced by the soil type, but the responsible factors have not been identified so far. Increasing temperature results in an accelerated degradation, whereas humidity has little effect on decomposition (except at the extremes of dried or flooded). However, the form of N fertilizer applied with GTU is important; the presence of urea provides a slower breakdown and better inhibitory effect than the combination of GTU with ammonium sulfate (AS) [7, 8]. The reason for this is not known.

In incubation experiments, the combination of U/GTU proved to be especially effective [7, 8]. At a rate of 100 kg N/ha, 10 kg/ha of GTU performed as well as 15 kg DCD/ha. The inhibitory effects of U/GTU were similar to the efficiency of the combination of AS/DCD. The objective of the following experiments was to confirm these described effects in pot experiments, with emphasis on testing the combination of urea with 10% of fertilizer-N as GTU. The efficiency of the nitrification inhibitors was measured by the amount of leached nitrate and by the amount of remaining nitrate utilized by plants.

Materials and methods

Inhibitors: TDZ, GTU (SKW Trostberg), DCD (Merck). Soil characteristics are given in Table 1. The soils were collected fresh from the fields, air-dried to about 40% water holding capacity (WHC), sieved to 1 cm and filled in 5 l Mitscherlich pots. The following amounts of soil fresh matter (FM) were used: 1985 5 kg Dürnast soil + 1 kg quartz sand; 1986 6 kg Dürnast soil without quartz sand, 5.5 kg Hohenbachern soil and 5.0 kg Mintraching soil. Basic dressing was given in sufficient amounts: 1.0 g P_2O_5 (1985) or 0.75 g P_2O_5 (1986) and 1.2 g K_2O/pot. The experiments were run with four replications. The fertilizers were incorporated into the 2 upper thirds of the soil (1985 as solution, 1986 as fertilizer granules). After N application the soil was initially moistened up to 100% WHC and preincubated at 17–25°C in the greenhouse, maintaining the moisture content at about 60% of WHC. The percolation was performed by adding water in several applications equivalent to 80 mm (1985) or 90 mm rainfall (1986) at 3 and 5 weeks after fertilizer application. The soil leachate was collected after 12 h and stored at −15°C until analysis.

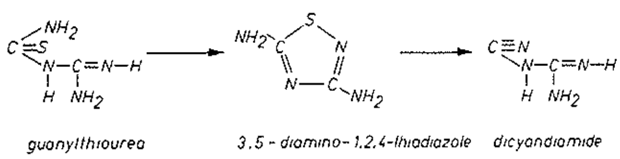

Fig. 1. Decomposition of GTU.

After percolation, oats (var. Pirol) were sown after restoration of aerobic soil conditions. The plants were grown at out-door temperatures and the pots were watered to 60% WHC daily (e.g. soil Dürnast 60% WHC = 30 kPa). After harvest at threshing-maturity, the soil was sieved (1 cm), returned to the pots, and Lolium perenne was sown as a second crop. Two cuts of the grass were harvested after it had grown to 15 cm height.

Nitrate in the percolation water was analyzed directly using HPLC [13]. Total nitrogen analysis of soils and plants was run according to Kjeldahl: 5 h digestion with conc. H_2SO_4 and 'Selen-Reagens' tablets (Merck) as catalyst at 220°C; distillation in closed apparature after neutralization with conc. NaOH, using boric acid as NH_3-trap; titration with 0.01 n H_2SO_4.

Results

Nitrate leaching

In the 1985 greenhouse study, 30–48% of the nitrogen applied was leached from the uncropped pots. In the case of AS, considerably less leaching occurred than with urea (Table 2). Both DCD and GTU proved to be very efficient inhibitors in Dürn-

Table 1. Soil properties

Soil	pH $CaCl_2$	C	N	Clay	Silt	$CaCO_3$
			(%)			
Dürnast loess brown earth	6.4	1.11	0.12	20	66	0.1
Mintraching humic sandy clay	7.3	4.40	0.49	35	16	10.0
Hohenbachern brown earth from tertiary sand	5.7	1.10	0.12	12	29	0

Table 2. Leaching of nitrate (mg N/pot) in pot experiments with various N fertilizers and nitrification inhibitors, 1985. (Application of 1200 mg N/pot including inhibitor-N, Dürnast soil)

Inhibitor (mg/pot)	Ammonium sulfate I	Ammonium sulfate II	Urea I	Urea II
None	406a	409b	578a	565a
180 DCD	119b	182bc	239b	393b
120 GTU	112b	154c	106c	150c
LSD 5%	30	33	45	44

I = percolation 3 weeks after fertilizer application, before sowing; II = percolation 5 weeks after fertilizer application, before sowing.
Means within a column followed by different letters are significantly different at the p = 0.05 level.

Table 3. Leaching of nitrate (mg N/pot) in pot experiments with various soils and nitrification inhibitors, 1986. (Urea application 800 mg N/pot including inhibitor-N)

Inhibitor (mg/pot)	Hohenbachern I	Hohenbachern II	Mintraching I	Mintraching II	Dürnast I	Dürnast II
none	482a	463a	429a	500a	425a	430a
180 DCD	212b	446a	238b	417b	233b	363b
120 GTU	176bc	341c	385a	507a	178b	272c
LSD 5%	69	54	54	72	66	52

I = percolation 3 weeks after fertilizer application, before sowing; II = percolation 5 weeks after fertilizer application, before sowing.
Means within a column followed by different letters are significantly different at the p = 0.05 level.

ast soil. The superiority of GTU was more apparent in combination with urea than AS; even after a 5-week period of preincubation before percolation only 10% of the nitrogen applied was leached as nitrate compared to 30% in the case of U/DCD or 50% without inhibitor. In the 1986 experiment no AS treatments were included, but a shallow sandy soil (Hohenbachern) and a highly organic soil (Mintraching) were used in addition to the loess Dürnast soil. Percolation was very effective since in all soils 50–60% of the urea without inhibitor was leached as nitrate (Table 3). GTU did not show any effect in the Mintraching soil while DCD had an effect. A prolonged inhibition by GTU was observed in Hohenbachern soil where N losses after 5 weeks were reduced by 20% in the case of GTU, but not in the case of DCD. The results with Dürnast soil correspond to those of the preceding year, though the application rate of DCD was reduced from 36 mg/kg soil to 24 and GTU from 24 mg/kg to 13. The amounts of NH_4-N, GTU and TDZ in the leachates were negligible, but DCD was leached in amounts up to 20% of the applied DCD or GTU [7].

Yields and N uptake

The oat yields and N uptake reflected losses of N due to leaching. The nitrogen remaining in the soil was utilized at 90–100%, thus essentially all the fertilizer nitrogen which had not been leached was taken up by the plants (Tables 4 and 5). In 1986, Dürnast soil showed significantly higher total yields and N uptake with U/GTU than with

Table 4. Yields and N uptake of oats in pot experiments with various N fertilizers and nitrification inhibitors, 1985. (Application of 1200 mg N/pot including inhibitor-N, Dürnast soil)

N source	Inhibitor (mg/pot)	Total yield (g dry m./pot) I	Total yield II	Grain yield (g fresh m./pot) I	Grain yield II	N uptake (mg N/pot) I	N uptake II
Ammonium Sulfate	none	101b	99ab	53b	54bc	783b	723b
	180 DCD	110c	108c	60c	60d	975d	922c
	120 GTU	107c	105bc	59c	58cd	998d	954c
Urea	none	87a	92a	42a	47a	612a	643a
	180 DCD	105bc	100b	57bc	52b	853c	754b
	120 GTU	110c	108c	60c	59d	972d	935c
LSD 5%		5.8	7.1	3.9	4.3	55	61

I = percolation 3 weeks after fertilizer application.
II = percolation 5 weeks after fertilizer application.
Means within a column followed by different letters are significantly different at the p = 0.05 level.

Table 5. Yields and N uptake of oats in pot experiments with various soils and nitrification inhibitors, 1986. (Urea application 800 mg N/pot including inhibitor-N)

Soil	Inhibitor (mg/pot)	Total yield (dry m./pot)		Grain yield (g fresh m./pot)		N uptake (mg N/pot)	
		I	II	I	II	I	II
Hohenbachern	none	41.2c	40.4b	19.7b	19.7b	299c	281b
	120 DCD	65.8b	41.8b	35.4a	19.9b	514b	285b
	80 GTU	71.9a	58.4a	38.7a	30.2a	605a	446a
LSD 5%		5.1	7.0	3.9	3.8	54	57
Mintraching	none	60.2b	48.8b	29.9b	23.1b	422c	322b
	120 DCD	76.7a	58.6a	39.7a	28.7a	641a	400a
	80 GTU	66.5b	47.7b	32.7b	23.0b	491b	338b
LSD 5%		6.9	6.5	3.9	3.5	64	50
Dürnast	none	56.6c	51.9c	27.9c	25.3c	388c	363c
	120 DCD	70.1b	56.9b	37.4b	30.4b	570b	442b
	80 GTU	76.5a	69.7a	41.0ab	37.4a	643a	555a
LSD 5%		6.3	7.4	5.7	4.4	76	63

I = percolation 3 weeks after fertilizer application.
II = percolation 5 weeks after fertilizer application.
Means within a column for each soil followed by different letters are significantly different at the $p = 0.05$ level.

U/DCD already after 3 weeks, in 1985 only after 5 weeks. With Mintraching soil, GTU failed to increase yields but DCD gave good effects. Largest differences were observed with grain yields in Hohenbachern soil: with percolation at 3 weeks the grain yield was doubled by using U/GTU instead of urea alone, and if leached at 5 weeks a 50% higher yield was still obtained. The subsequent crop Lolium perenne and the analysis of roots of the 1986 experiment did not reveal any differences between treatments on any soil [7].

Discussion

The soil type had a strong effect on the performance of the inhibitors. In the loess Dürnast soil, U/GTU generally showed significantly less nitrate leaching and more plant yield than U/DCD. These results agree with earlier degradation and incubation experiments [7, 8]; in the latter case GTU had a much better inhibitory effect than DCD. Additionally, combinations of DCD and GTU were examined in incubation and greenhouse experiments [7]; these data are not presented, because no synergistic effects of the combination DCD/GTU were observed. The two other soils reacted very differently; in Mintraching soil with high organic matter content, degradation of GTU was extremely slow, and the inhibitor did not show any effect. This is difficult to explain. To a certain extent, the structure of the granules might have been responsible [7], or perhaps GTU was adsorbed to the organic matter and could not reach the active sites of nitrification. In a different study, superiority of DCD over GTU was found [4], with application of very low amounts of inhibitors (10 ppm).

The sandy Hohenbachern soil, despite a rapid decomposition of GTU observed in degradation experiments, gave the most conspicuous differences, because the physical properties of this soil caused greater N losses than Dürnast soil. In this soil, DCD did not show any effect after 5 weeks, whereas GTU significantly reduced the leaching of N at this period and effected a highly significant increase in yield. Further research is needed to establish the proper employment of GTU and to determine conditions where GTU is superior to DCD. By the three-step inhibition of nitrification, from GTU via TDZ to DCD, a greater efficiency of GTU than of DCD can be expected in most cases – which is expressed for example in the lower application rate of GTU (e.g. 10 kg/ha) compared to DCD (e.g. 15 kg/ha).

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