

Ability of nitrapyrin, dicyandiamide and acetylene to retard nitrification in a mineral and an organic soil

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Abstract

Laboratory experiments were conducted to evaluate the efficacy of nitrapyrin, dicyandiamide (DCD) and acetylene (C_2H_2) as nitrification inhibitors in a silt loam and organic soil with and without added NH_4 . Nitrapyrin ($8 \mu g/g$ soil) and DCD ($20 \mu g/g$ soil) were very effective in retarding nitrification of NH_4 -N in the silt loam soil during 14 days of aerobic incubation at $30^\circ C$. However neither nitrapyrin ($20 \mu g/g$ soil) nor DCD (20 or $100 \mu g/g$ soil) were effective in retarding NO_3 production in the organic soil not amended with NH_4 . Dicyandiamide was moderately effective in retarding nitrification (39% inhibition) at $100 \mu g/g$ concentration but nitrapyrin at $20 \mu g/g$ rate had little effect (8% inhibition) on nitrification in the organic soil amended with NH_4 . In a separate experiment C_2H_2 was a very effective inhibitor in both soils when present in the flask atmosphere at 0.1% or 1% (v/v).

Introduction

The efficacy of synthetic organochlorine nitrification inhibitors such as nitrapyrin [2-chloro-6-(trichloromethyl) pyridine] is strongly influenced by soil organic matter (Hendrickson and Keeney, 1979; Keeney, 1980). However, little is known of the interaction between compounds such as C_2H_2 or DCD and organic matter. Acetylene, which blocks N_2O reduction to N_2 by denitrifiers, also is an effective inhibitor of nitrification (Bremner and Blackmer, 1979; Walter *et al.*, 1979). Dicyandiamide, which has long been known as a nitrification inhibitor (Amberger, 1981; Reddy, 1964) is marketed by SKW Trostberg AG, Trostberg, West Germany under the trade name Didin (Hauck and Behnke, 1981).

The objective of this study was to compare the effectiveness of nitrapyrin, C_2H_2 , and DCD, nitrification inhibitors that have widely differing chemical and physical properties, in a mineral and an organic soil.

Materials and methods

The soils used (Table 1) were surface (0 to 15 cm) samples of Plano silt loam (Typic Arguidoll) and an organic soil (Histosol, Sapristis). The samples were air dried and crushed to pass a 2-mm sieve before use. For the analyses reported in Table 1, pH in water was measured by a glass electrode, Organic C was determined on 100 mesh ground samples (Harris and Adams, 1979) and exchangeable NH_4 and ($NO_2 + NO_3$)-N were determined on 2 M KCl

Table 1. Analyses of soils

Soil	pH ^a	Organic C	Mineral N ^b ($\mu g/g$)	
			NH_4	NO_3
Plano silt loam	7.0	1.4	7	11
Histosol	6.8	40.0	13	253

^a Soil pH was measured using soil to water ratio of 1:2 for the Plano silt loam and 1:4 for the organic soil.

^b For the experiments evaluating nitrapyrin and DCD.

Table 2. Effects of nitrapyrin and DCD on nitrification of soil N in a mineral and an organic soil. Values express mineral N content ($\mu\text{g/g}$) at 14 days

Treatment	Plano silt loam			Histosol		
	NH ₄	NO ₃	Total	NH ₄	NO ₃	Total
No amendment ^a	4	52	56	10	433	443
Nitrapyrin (8 $\mu\text{g/g}$)	39	14	53	8	426	434
No amendment ^b	4	37	41	6	461	467
DCD (20 $\mu\text{g/g}$)	23	24	47	— ^c	—	—
Nitrapyrin (20 $\mu\text{g/g}$)	—	—	—	7	466	473
DCD (50 $\mu\text{g/g}$)	—	—	—	8	478	486
DCD (100 $\mu\text{g/g}$)	—	—	—	16	466	482

^{a,b} Experiments done at two separate times.^c Not done.

extracts by steam distillation (Bremner and Keeney, 1965).

Evaluation of nitrapyrin and DCD

Soil samples (5 g) were placed in 125 ml Erlenmeyer flasks and treated with water or with (NH₄)₂SO₄ (200 $\mu\text{g/g}$ NH₄-N); and nitrapyrin (0, 8 or 20 $\mu\text{g/g}$), or DCD (0, 20 or 100 $\mu\text{g/g}$) were added in aqueous solutions. The water content of the soil samples was brought to -33 kPa. The flasks were covered with aluminium foil caps having a 1-mm central hole (for aeration) and placed in a constant temperature cabinet at 30°C in a humidified atmosphere. Each treatment was in duplicate. After 14 days, inorganic N in the samples was analysed as described earlier.

Table 3. Effects of nitrapyrin and DCD on nitrification in soils treated with ammonium sulfate (AS, 200 $\mu\text{g/g}$ soil). Values express mineral N content ($\mu\text{g/g}$) at 14 days

Treatment	Plano silt loam			Histosol		
	NH ₄	NO ₃	Total	NH ₄	NO ₃	Total
AS ^a	28	207	235	8	623	631
AS + Nitrapyrin (8 $\mu\text{g/g}$)	234	15	249	7	624	631
AS ^b	43	180	223	8	675	683
AS + Nitrapyrin (8 $\mu\text{g/g}$)	234	4	238	— ^c	—	—
AS + DCD (20 $\mu\text{g/g}$)	208	23	231	—	—	—
AS + Nitrapyrin (20 $\mu\text{g/g}$)	—	—	—	29	639	668
AS + DCD (10 $\mu\text{g/g}$)	—	—	—	157	508	665

^{a,b} Experiments conducted at two separate times.^c Not done.

Evaluation of C₂H₂

Soil samples (10 g) were incubated in 125-ml Erlenmeyer flasks. Water was added to the samples after amendment to bring the soil moisture content to -33 kPa with NH₄-N (0 or 100 $\mu\text{g/g}$) as (NH₄)₂SO₄. The flasks were stoppered with rubber septa. In the plus C₂H₂ treatments, 0.1 or 1% volume of air in the flasks was replaced by pure (99.9%) C₂H₂ by a syringe. The samples were incubated at 25°C for 1 week. Atmospheres in the flasks were replaced at 4 days by humidified air and appropriate amounts of C₂H₂ added. Preliminary experiments showed that the rubber septa used were leakproof, and the concentrations of C₂H₂ inside the flasks stoppered with the septum was maintained during the duration of the experiment. After 1 week, the soil samples were analysed for inorganic N as described earlier.

Inhibition of nitrification was calculated by the difference between the NO₃-N produced during incubation in the control and inhibitor-treated soils (Bundy and Bremner, 1973).

Results and discussion

Results on the effects of nitrapyrin, DCD and C₂H₂ on nitrification of soil or added ammonium are presented in Tables 2, 3 and 4. These results indicate that total mineral N balance in the Plano soil and in the Histosol with and without inhibitor treatments were close, suggesting little loss of mineral N due to denitrification during the study.

Table 4. Effects of C₂H₂ on nitrification of soil and added ammonium in soils. Values express mineral N content (µg/g) at 7 days

NH ₄ -N added (µg/g)	C ₂ H ₂ (% v/v)			
	0	0.1	1.0	
<i>Plano silt loam</i> ^a				
0	NH ₄ -N	6	39	37
	NO ₃	41	13	12
	Total	47	52	49
100	NH ₄	79	127	127
	NO ₃	60	13	12
	Total	139	140	139
<i>Histosol</i> ^b				
0	NH ₄	13	189	196
	NO ₃	444	262	264
	Total	457	451	460
100	NH ₄	71	295	295
	NO ₃	494	266	263
	Total	565	561	558

^a The soil contained NH₄, 9 µg/g; NO₃, 12 µg/g at the start of the experiment.

^b The soil contained NH₄ 16 µg/g; NO₃, 268 µg/g at the start of the experiment.

With the mineral soil, nitrapyrin was considerably more effective in inhibiting nitrification of indigenous ammonium in the soil than DCD but both were equally effective with added NH₄ (Table 2, 3 and 5). However, neither compound was effective with the Histosol. In contrast, C₂H₂ was an

Table 5. Nitrification inhibition (%)^c by nitrapyrin, DCD or C₂H₂

Inhibitor	Compound	Rate	Plano silt loam		Histosol	
			0 ^a	+ NH ₄ ^b	0 ^a	+ NH ₄
Nitrapyrin ^c		8 µg/g	93	98	4	0
		20 µg/g	—	—	0	8
DCD ^c		20 µg/g	50	93	—	—
		100 µg/g	—	—	0	39
C ₂ H ₂ ^d		0.1% v/v	97	98	100	100
		0.1% v/v	100	100	100	100

^a Non-amended soil.

^b Soil amended with 200 µg NH₄-N/g soil for evaluation of nitrapyrin and DCD, and with 100 µg NH₄-N/g soil for evaluating C₂H₂.

^c 14 days at 30°C.

^d 7 days at 25°C.

^e % inhibition of nitrification =

$$\frac{(\text{NO}_3\text{-N produced in control soil}) - (\text{NO}_3\text{-N produced in inhibitor-treated soil})}{(\text{NO}_3\text{-N produced in control soil})} \times 100$$

extremely effective inhibitor of nitrification in both soils (Table 4 and 5).

The organic soil we used had an extremely rapid nitrification rate. This, coupled with high temperature (25 to 30°C) and optimum water and aeration status of the incubation procedure used, provided an extreme test of nitrification inhibitor efficacy.

It would appear that the sorption of nitrapyrin by organic matter was the probable reason for the ineffectiveness of this compound with the organic soil (Hendrickson and Keeney, 1979). We are not certain why DCD was ineffective in the Histosol. DCD could be rapidly degraded in this soil although Vilsmeier (1981) indicates that at 25°C about 50% of the added DCD remained after 2 weeks in a sandy loam soil. It is not strongly sorbed by soil constituents (Ashworth and Rodgers, 1981; Bock *et al.*, 1981) although the rate of DCD leaching was found to be inversely related to organic matter content (range 0.7 to 5.3% organic matter) in six soils studied by Bock *et al.* (1981).

The effectiveness of C₂H₂ in the organic soil is related to the fact that this compound, added as a gas, can completely permeate the soil matrix. Further, the experimental design was such that it was replaced at day four and thus degradation in the soil was not a major factor.

These results show that the inhibitors are differentially effective in mineral vs. organic soil, which could be due to differential retention and mobility in the two soils. An ideal compound might be a 'slow release' inhibitor with a high vapour pressure and low organic matter retention characteristics.

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