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EFFECTS OF NITRIFICATION INHIBITORS ON NITROGEN TRANSFORMATIONS, OTHER THAN NITRIFICATION, IN SOILS[1]

K. L. Sahrawat

International Crops Research Institute for the Semi-Arid Tropics
ICRISAT Patancheru P.O.
Andhra Pradesh 502 324, India

I. INTRODUCTION

Interest in nitrification inhibitors stems from the fact that retardation of nitrification reduces loss of nitrogen by leaching and denitrification following nitrification. This helps in some situations to achieve more efficient use of nitrogen for crop production and may also help in minimizing fertilizer nitrogen-related environmental stresses, especially accumulation of nitrate in surface and ground waters. Nitrification is generally used to mean biological oxidation of ammonium to nitrate via nitrite effected, respectively, by *Nitrosomonas* and *Nitrobacter* species of nitrifying bacteria, although nitrification inhibitors are defined as compounds or materials that specifically retard the oxidation of ammonium to nitrite without

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affecting the subsequent oxidation of nitrite to nitrate. Inhibition of nitrification is referred to as retardation of nitrification because complete inhibition is seldom achieved with the use of nitrification inhibitors.

The literature on nitrification inhibitors is very extensive (e.g., see Gasser, 1970; Prasad *et al.*, 1971; Hauck, 1972, 1983, 1984; Huber *et al.*, 1977; Meisinger *et al.*, 1980; Sahrawat, 1980, 1986; Hauck and Behnke, 1981; Mulvaney and Bremner, 1981; Slangen and Kerkhoff, 1984; Sahrawat and Keeney, 1984, 1985; Amberger, 1986). These reviews cover various aspects of the effects of nitrification inhibitors on (i) retardation of nitrification in soil, and (ii) crop production and some aspects of crop quality (e.g., see Sahrawat and Keeney, 1984).

The interest in nitrification inhibitors followed the development of nitrapyrin [2-chloro-6-(trichloromethyl) pyridine] by the Dow Chemical Company of the United States as an effective inhibitor of nitrification (Goring, 1962a,b).

Research has suggested that in addition to retarding nitrification, nitrification inhibitors may affect certain other processes of the nitrogen cycle in soils such as mineralization–immobilization, nitrous oxide production, ammonia volatilization, and denitrification (e.g., see Table I). The capacity of nitrification inhibitors to affect these processes depends on their bioactivity in soil, which is affected by soil texture, temperature, and the amount of inhibitor added. The half-lives of nitrification inhibitors such as nitrapyrin may vary from a few days to several weeks depending on the rate of application, soil type, and season (temperature) (e.g., see Meisinger *et al.*, 1980; Sahrawat, 1980).

This review summarizes the literature on the effects of nitrification inhibitors on nitrogen transformations other than nitrification in soil and identifies future directions for research. This field of research is developing in importance because of increasing interest in the use of these chemicals.

II. EFFECTS OF NITRIFICATION INHIBITORS ON PHYSICAL AND CHEMICAL PROCESSES RELEVANT TO NITROGEN TRANSFORMATIONS

Since retardation of nitrification increases the persistence of ammonium in soils, it must be expected that retardation of nitrification affects ammonium nitrogen transformation processes such as fixation or adsorption and volatilization in some situations. Also, retardation of nitrification may result overall in less movement and transport of mineral nitrogen because of higher NH_4/NO_3 ratios in soils caused by retardation of nitrification (e.g., see Sahrawat and Keeney, 1984).

Table I

Recent References on the Effects of Nitrification Inhibitors on Nitrogen Transformations, Other Than Nitrification, in Soils

Aspect of N transformation processes	References
Physical and chemical processes	
N transport and movement	Huber *et al.* (1969); Keeney *et al.* (1979); Owens (1981); Papendick and Engibous (1980); Hergert and Wiese (1980); Onken (1980); Timmons (1984)
Ammonium fixation and release	Giri *et al.* (1982); Juma and Paul (1983); Aulakh and Rennie (1984)
Ammonia volatilization	Cornforth and Chasney (1971); Bundy and Bremner (1974); Smith and Chalk (1978, 1980); Jain *et al.* (1981); Rodgers (1983); Simpson *et al.* (1985); Magalhaes and Chalk (1987); Prakasa Rao and Puttanna (1987)
Biological processes	
ineralization and immobilization	Dubey and Rodriguez (1970); Laskowksi *et al.* (1975); Malhi and Nyborg (1979a, 1983); Juma and Paul (1983, 1984); Aulakh and Rennie (1984)
Denitrification	Mitsui *et al.* (1964); Sandhu and Moraghan (1972); Henninger and Bollag (1976); McElhannon and Mills (1981); Notton *et al.* (1979); Yeomans and Bremner (1985a,b); Bremner and Yeomans (1986); Mills (1984); Mills and McElhannon (1984)
Nitrous oxide production	Bremner and Blackmer (1978, 1979); Freney *et al.* (1979); Smith and Chalk (1978, 1980); Bremner *et al.* (1981); Aulakh *et al.* (1984); Magalhaes *et al.* (1984); Yeomans and Bremner (1985a,b); Casella *et al.* (1986); Bremner and Yeomans (1986); Davidson *et al.* (1986); Magalhaes and Chalk (1987)
Urea hydrolysis	Goring (1962b); Bremner and Douglas (1971); Bundy and Bremner (1974); Bremner and Bundy (1976); Reddy and Prasad (1975); Ashworth *et al.* (1977, 1979, 1980); Amberger and Vilsmeier (1979); Guthrie and Bomke (1981); Rodgers (1983); Sahrawat (1979a,b); Mishra and Flaig (1979); Mishra *et al.* (1980); Lethbridge and Burns (1976); Malhi and Nyborg (1979b); Goos (1985)

A. TRANSPORT AND MOVEMENT OF NITROGEN

Keeping nitrogen in the ammonium form by retarding nitrification reduces movement of mineral nitrogen because (i) ammonium is retained by soil particles and thus is less mobile and (ii) if less nitrate is formed, this results in reduced amounts of nitrate N leached. For example, in a

3-year study Huber *et al.* (1969) showed that in the field inhibition of nitrification of fall-applied ammonium sulfate with nitrapyrin (0.56 kg/ha) prevented the movement of applied nitrogen below a depth of 30.5 cm (Table II). These results show that the inhibition of nitrification reduced the amounts of nitrate formed and its subsequent leaching in the soil profile. A greater proportion of mineral N was present in the ammonium form in the inhibitor-treated plots.

Keeney *et al.* (1979) found that nitrapyrin inhibited nitrification of ammonium in a loamy sand soil and also reduced the amounts of nitrate leached in soil columns over 2–5 weeks. However, by 20 weeks, the period for which the experiment was run, the amounts of nitrate leached were similar in soil columns with and without nitrification inhibitor treatment. This might have been due to degradation of nitrapyrin. Similarly, Owens (1981) showed that nitrapyrin reduced the amounts of mineral N (mostly nitrate) leached in 1-m-long soil columns. After 91 days, 1.0 and 9.7% of the applied urea nitrogen had leached from nitrapyrin-treated and untreated soil cores; however, after 144 days, 41.9 and 53.0%, respectively, of applied N had leached.

Studies in the United States on the effect of nitrapyrin on transformations and movement of fertilizer nitrogen in soils indicated that in some situations it reduced the movement of fertilizer nitrogen over winter or during irrigation (Hergert and Wiese, 1980; Onken, 1980; Papendick and Engibous, 1980; Timmons, 1984). In a 3-year field lysimeter study, Timmons, (1984)

Table II

Extractable Ammonium and Nitrate N Content (kg/ha) in Southwick Silt Loam Soil in the Spring Following Fall N Fertilization with and without Nitrapyrin[a,b]

	NO_3 N at depth (cm)			NH_4 N at depth (cm)		
Treatment	0.0–30.5	30.5–61.0	Total	0.0–30.5	30.5–61.0	Total
Control	17.3	18.9	36.2	2.9	8.3	11.2
Calcium nitrate	21.2	18.9	40.1	8.5	5.4	13.9
Calcium nitrate plus nitrapyrin	19.3	22.5	41.8	11.3	7.6	18.9
Ammonium sulfate	35.3	20.7	56.0	8.8	8.1	16.9
Ammonium sulfate plus nitrapyrin	28.7	22.2	50.9	27.6	9.2	36.8

[a] From Huber *et al.* (1969). The study was conducted in the fall of 1965, 1966, and 1967. Data are average of 3 years.

[b] Nitrogen was applied at the rate of 67.5 kg N/ha in the fall of 1965 and 1966, and 84 kg N/ha in the fall of 1967. Nitrapyrin was added annually at a rate of 0.56 kg/ha.

found that nitrapyrin application with urea reduced the los of NO_3 N leached at the 1.2-m depth in soil planted to corn (*Zea mays* L.) (Table III).

In a 6-year lysimeter study, Owens (1987) found that nitrapyrin (1.12 kg/ha) application with urea (336 kg N/ha) reduced the loss of inorganic N in percolation water from Rayne silt loam (fine loamy, mixed, mesic; Typic Hapludult) planted to no-tillage corn. The average annual N loss by leaching in the untreated lysimeter was 160 kg N/ha, which was reduced to 117 kg N/ha by nitrapyrin application. Nitrapyrin was found to be effective in reducing the leaching loss of inorganic N in spring, summer, autumn, and winter (Table IV).

Table III

Leaching Loss of Nitrate N in a Field Lysimeter Sandy Loam Soil (Typic Hapludoll) Fertilized with Urea, with and without Nitrapyrin[a]

	Treatment[b]	
Year	Urea	Urea plus Nitrapyrin
	Percolation (mm)	
1977	337	313
1978	233	236
1979	218	234
Average	263	261
	NO_3 N leached (kg/ha)	
1977	194	148
1978	161	157
1979	127	142
Average	161	149
	Flow-weighted NO_3 N Conc[c] (mmol/liter)	
1977	4.1	3.4
1978	4.9	4.7
1979	4.2	4.3
Average	4.4	4.1

[a] From Timmons (1984). Each value is an average of three replications measured at 1.2-m depth.

[b] Lysimeters were fertilized with 224 kg urea N/ha before planting to corn and nitrapyrin was added at the rate of 0.56 kg/ha.

[c] Flow-weighted concentration is total NO_3 N leached divided by total water percolated and converted to mmol/liter.

Table IV

Effect of Nitrapyrin on Nitrogen Loss in Percolation Water from Rayne Silt Loam (Typic Hapludult) in Lysimeters Fertilized with Urea and Planted to No-Tillage Corn[a]

		Inorganic N loss[b] (kg N/ha)				
Lysimeter	Treatment	Spring	Summer	Autumn	Winter	Annual
A	Urea	66.6	12.0	18.8	62.6	160.0
B	Urea plus nitrapyrin	51.7	10.2	12.6	45.2	119.7
C	Urea plus nitrapyrin	49.3	9.8	14.0	40.9	114.0

[a] From Owens (1987); results presented are averages of 6 years' data, 1978–1984. Urea was applied at a rate of 336 kg N/ha and nitrapyrin at the rate of 1.12 kg/ha annually.

[b] Spring, April–June; Summer, July–September; Autumn, October–December; Winter, January–March.

B. AMMONIUM FIXATION AND RELEASE

The retardation of nitrification can enhance immobilization of fertilizer nitrogen because the persistence of ammonium increases (i) its incorporation in the organic nitrogen fraction or (ii) its migration to fixed or nonexchangeable sites on clay minerals. For example, Juma and Paul (1983) found that under field conditions treatment of ^{15}N-aqueous NH_3 and ^{15}N-urea with a nitrification inhibitor, ATC (4-amino-1,2,4-triazole), caused enhanced recovery of fertilizer N in the soil surface layer (52–55% versus 28–30%). Between 5 and 8% of the fertilizer N was recovered in the nonexchangeable ammonium form in the A horizon of the soil treated with ATC as opposed to about 1% in the non-ATC treatments (Table V). Laboratory study these soil samples further revealed that the nonexchangeable $^{15}NH_4$ was released at rates equivalent to a half-life of 38 weeks and the rate constant was 0.018/week at 28 ± 1°C at a soil water potential of − 34 kPa (kPascal). The clay fraction of the soil, consisting of mica, vermiculite, and smectites, contained 49% of the labeled nonexchangeable NH_4 whereas the coarse silt fraction accounted for 26% of the labeled nonexchangeable NH_4.

Aulakh and Rennie (1984) showed that nitrapyrin did not increase the fixation of NH_4 initially, but the release of recently fixed NH_4 was decreased and delayed by nitrapyrin application in a 2-year study of fall-applied ^{15}N-labeled urea in Canadian chernozemic soils (Typic Udic Haploborrolls) (Table VI). In another experiment, nitrapyrin application significantly increased the amount of fertilizer urea recovered as fixed NH_4 after 8 months of application to a clay loam soil (see Table XV). In some situations the changes in the amounts of fixed NH_4 could influence N loss and availability to plants.

Table V

Percentage Recovery of ^{15}N-Labeled Aqueous Ammonia and Urea in a Loam Soil (0.43% total N, pH 7.4) with and without ATC Nitrification Inhibitor after Harvest of the Wheat Crop[a,b]

N recovered in soil depth	Treatments			
	NH_4OH	NH_4OH + ATC	Urea	Urea + ATC
0–15 cm	28	56	31	52
15–30 cm	10	3	10	2
30–60 cm	2	1	2	1
Total	40	60	43	55
Nonexchangeable NH_4[c]	1	5	1	8

[a] From Juma and Paul (1983).

[b] The fertilizers were added at a rate of 56 kg N/ha and the inhibitor at a rate of 4% of fertilizer N. The ^{15}N excess of each fertilizer was 5.6%

[c] Nonexchangeable NH_4 expressed as percentage of the remaining ^{15}N.

C. AMMONIA VOLATILIZATION

Retardation of nitrification in soil results in accumulation of ammonium and higher soil pH (Cornforth and Chasney, 1971; Hauck and Bremner, 1969; Bundy and Bremner, 1974; Smith and Chalk, 1978; Magalhaes and Chalk, 1987), which are conducive to ammonia volatilization. In fact, Cornforth and Chasney (1971) showed in the field that application of AM (2-amino-4-chloro-6-methyl pyrimidine) nitrification inhibitor with ammonium sulfate (168 kg N/ha) increased the ammonia loss by volatilization

Table VI

Changes in Ammonium Fixation (kg N/ha) of Fall-Applied Urea in the Soil Profile to 30-cm Depth without and with Nitrapyrin Applied to Baline Lake Clay Loam Soil[a]

Sampling date	Treatment[b]	
	Urea	Urea + Nitrapyrin
30 September 1981	10.6	10.8
20 October 1981	8.6	9.7
1 December 1981	9.6	9.1
23 March 1982	6.9	7.4
27 April 1982	6.2	8.1
27 May 1982	1.0	4.6

[a] From Aulakh and Rennie (1984).

[b] Urea was applied at a rate of 100 kg N/ha and nitrapyrin at a rate of 1% of fertilizer N on 30 September 1981.

from bare soil. The inhibitor increased by nearly eightfold the amount of ammonia volatilized from grass-covered soils in comparison with the control during 28 days of study, and nearly 22 kg N/ha was lost as ammonia. Less ammonia was lost when unamended ammonium sulfate or urea was applied to grass rather than to bare plots.

Bundy and Bremner (1974) showed that nitrapyrin [2-chloro-6-(trichloromethyl) pyridine], ATC (4-amino-1,2,4-triazole) and CL-1580 (2,4-diamino-6-trichloromethyl-s-triazine) nitrification inhibitors retarded nitrification of urea in soil but increased the volatile loss of ammonia from soils in a laboratory study (Table VII). However, it should be mentioned that these losses were experienced when a sandy clay loam soil was treated with a relatively high rate of urea (400 μg N/g soil). This study, nevertheless, indicates the potential of high loss due to ammonia volatilization when nitrification inhibitors in conjunction with urea are surface-applied to coarse-textured calcareous soils. The increased ammonia volatilization from soils treated with nitrification inhibitors was due to the persistence of ammonium and higher soil pH (Table VIII), which created a soil environment conducive to ammonia volatilization.

In another laboratory study, Rodgers (1983) determined the loss by ammonia volatilization from three soils fertilized with urea prills or urea prills containing 7% by weight of DCD (dicyandiamide), a nitrification inhibitor. It was found that the volatile loss of ammonia was less when urea or urea and DCD was incorporated than when it was applied to the surface. Soil type influenced the volatile loss of ammonia during 4 weeks of testing. The volatile loss of ammonia from a soil that did not nitrify was not affected by DCD application but volatilization was increased in the two other soils (Table IX). In general, the soils were quite slow in nitrification, and by

Table VII

Effects of Three Nitrification Inhibitors on Nitrification and Volatile Loss of Ammonia from a Sandy Clay Loam Soil (pH 7.2; organic C 1.65%) at 14 Days of Incubation[a,b]

Inhibitor	Inhibition of nitrification (%)	Volatile loss as ammonia (% of urea N added)
None	—	9
Nitrapyrin	94	34
ATC	92	30
CL-1580	88	28

[a] From Bundy and Bremner (1974).

[b] Soil samples (10 g) were treated with 4 mg of urea N and with 0 or 100 μg of nitrification inhibitor and incubated at 30°C and 60% WHC (water holding capacity) moisture.

Table VIII

Effect of Nitrapyrin on Soil pH in a Sandy Clay Loam Soil Treated with Urea[a,b]

Time (days)	Soil pH (1:2.5 H_2O)	
	With nitrapyrin	Without nitrapyrin
0	7.2	7.2
2	8.2	8.0
4	8.2	7.3
6	8.2	6.3
8	8.1	6.2
10	8.0	6.1
12	8.0	6.2
14	8.0	6.2
21	7.5	6.2

[a] From Bundy and Bremner (1974).

[b] Soil samples (10 g) were treated with 4 mg of urea N and with 0 or 100 μg of nitrapyrin and incubated at 30°C and 60% WHC moisture.

4 weeks only 1–21% of the urea N added was recovered as nitrate N in soil samples not treated with DCD. The effects on ammonia volatilization due to retardation of nitrification in this study are not as dramatic as those obtained by Cornforth and Chasney (1971) in the field and Bundy and Bremner (1974) in the laboratory. These differences are probably due to the difference in nitrifying capacity of soils and persistence of ammonium in soil samples with and without the nitrification inhibitor treatment. Smith and Chalk (1978) found that in a calcareous soil treated with ammonia, nitrapyrin application only slightly increased the volatile loss of ammonia in 28 days. The volatile loss of ammonia amounted to 86 and 92 μg/g soil in treatments without and with nitrapyrin when the soil was fertilized with 1127 μg/g ammonia N. The pH of the nitrapyrin-treated soil was higher, as was the extractable NH_4 N, and nitrification was at a low ebb (Table X).

The losses due to ammonia volatilization by retardation of nitrification were similar and small in the studies reported by Rodgers (1983) and Smith and Chalk (1978) although they used high rates of urea application (Tables IX and X). This could additionally be due to the different method of urea application used by these researchers (soil incorporation) as opposed to Bundy and Bremner (1974). Also, Rodgers (1983) used urea prills and Bundy and Bremner (1974) applied urea solution to the soil surface, and this might have affected urea hydrolysis and subsequent nitrification. As

Table IX

Effect of Dicyandiamide (DCD) on Urea Transformations in Three Soils[a,b]

Soil	Form of urea N recovered	Treatment	
		Urea	Urea + DCD
Rothamsted (pH 5.2)	Urea N	0.0	0.0
	NH_4 N	77.8	78.2
	NO_2 N	0.0	0.0
	NO_3 N	1.0	0.5
	NH_3 N	15.4	14.6
Saxmundham (pH 7.7)	Urea N	0.0	0.0
	NH_4 N	72.4	74.9
	NO_2 N	2.6	0.1
	NO_3 N	20.9	2.1
	NH_3 N	9.2	11.8
Woburn (pH 5.4)	Urea N	0.0	0.0
	NH_4 N	56.2	58.9
	NO_2 N	0.8	0.0
	NO_3 N	16.0	2.0
	NH_3 N	31.2	37.3

[a] From Rodgers (1983).

[b] Soil samples (50 g) were treated with 50 mg urea N or urea containing 7.2% by weight DCD and incubated at 30°C under aerobic conditions for 4 weeks.

Table X

Effects of Nitrapyrin on Inorganic N and Gaseous N Evolution (μg N/g soil) from a Calcareous Soil (pH 8.5, organic C 1.3%) Treated with Ammonia[a,b]

Treatment	Soil pH	Inorganic N (28 days)			Gaseous N evolved (28 days)			
		NH_4^+	NO_3^-	NO_2^-	N_2	N_2O	$NO + NO_2$	NH_3
No nitrapyrin	7.8	792	70	154	76	57	9	86
Nitrapyrin	8.2	1012	44	0	13	0	1	92

[a] From Smith and Chalk (1978).

[b] Soil samples were incubated at 30°C and 0.33 bar soil water potential after treatment with 1127 μg ammonia N/g soil, and 0 to 10 μg nitrapyrin/g soil.

mentioned earlier, the soils in these studies differed greatly in their capacity to produce nitrate from hydrolyzed urea.

Simpson *et al.* (1985) studied the effects of phenylphosphorodiamidate (PPD), a urease inhibitor, and dicyandiamide, a nitrification inhibitor, on nitrogen losses, transformations, and recovery of nitrogen, when urea was applied to a flooded rice field. It was found that although PPD delayed urea hydrolysis and decreased loss via ammonia volatilization, DCD, the nitrification inhibitor, had no significant effect on nitrate concentrations in the flood water and ammonia loss. Of the 80 kg of urea N added, 20.6% was lost through ammonia volatilization from the control, followed by 18.8% from the urea plus DCD treatment, and 12.5% from the urea plus PPD treatment during the 11 days after application of the fertilizer (Table XI). These results show that DCD was not effective in inhibiting nitrification in the flooded soil, in contrast to its effectiveness as a nitrification inhibitor in aerobic soils (Amberger, 1986). The pattern of ammonia loss from the urea plus PPD treatment was very different from that of the

Table XI

Effects of DCD and Phenylphosphorodiamidate (PPD) on Ammonia Volatilization Losses (kg N/ha/day) from Flooded Clay Soil (Pelloxerert, pH 8.2)[a,b]

Days after urea application	Treatment		
	Urea	Urea + DCD	Urea + PPD
0	0.11	0.28	0.00
1	2.70	2.24	0.07
2	3.00	1.32	0.05
3	3.67	2.38	0.22
4	1.00	1.06	0.20
5	1.08	0.96	0.50
6	1.30	1.12	0.94
7	1.12	1.47	1.88
8	0.49	1.11	1.74
9	0.77	1.14	1.35
10	0.86	1.43	1.81
11	0.39	0.56	1.21
Total loss	16.49	15.07	9.97
Loss as % of applied N	20.6	18.8	12.5

[a] From Simpson *et al.* (1985).

[b] Prilled urea applied at the rate of 80 kg N/ha by uniformly broadcasting into the flood water. DCD was added at the rate of 10% urea N and PPD at the rate of 1% of urea N (w/w).

Table XIII

The Effects of Nitrification Inhibitors on the Release of Mineral N over the Winter in Malmo Silty Clay Loam Soil (pH 6.0; O.M. 9.7%) in 1978–1979[a]

	NH_4 N and NO_3 N in the 0–30-cm layer[c]								
	NH_4 N (kg/ha)			NO_3 N (kg/ha)			(NH_4 + NO_3) N (kg/ha		
Treatment[b]	27 Oct	16 Mar	10 May	27 Oct	16 Mar	10 May	27 Oct	16 Mar	10 M
Control	14	22 c	22 b	14	60 a	18 a	28	82 a	40 b
ATC	—	30 b	36 a	—	33 b	19 a	—	63 b	55 a
Nitrapyrin	—	25 bc	24 b	—	56 a	16 a	—	81 a	40 b
CS_2	—	38 a	40 a	—	21 c	19 a	—	59 b	59 a

[a] From Malhi and Nyborg (1983).

[b] The nitrification inhibitors were added at a rate of 22 kg/ha. ATC and nitrapyrin were mix into the soil to a depth of 10 cm, and carbon disulfide (CS_2) was injected 10 cm deep in bands cm apart.

[c] In each column, the values not followed by the same letter are significantly different (p = 0.0

without ATC nitrification inhibitor (Juma and Paul, 1983) to study the effect of the nitrification inhibitor on N mineralization during 2 weeks of incubation at 28 ± 1°C and − 34 kPa soil moisture tension in the laboratory and on NH_4 released during a 10-day incubation of fumigated soil. It was found that although the nitrification inhibitor did not affect the mineral N released during 2 weeks of incubation, the amounts of NH_4 N released in fumigated soils were higher in the inhibitor-treated samples. The extractability ratios (ratio of atom percentage ^{15}N excess of extracted N to atom percentage ^{15}N excess of total N) were higher for the samples treated with the nitrification inhibitor compared to those treated with fertilizer alone.

Juma and Paul (1983) made a detailed study of the effect of ATC on immobilization of ^{15}N-labeled aqueous ammonia and urea N and found that ATC caused a greater immobilization of fertilizer ^{15}N (see Table V) and also increased the rate of release of ^{15}N-labeled microbial biomass following fumigation and incubation for 12 weeks (Table XIV). Aulakh and Rennie (1984) found that immobilization of fall-applied labeled urea and KNO_3 was minimal under fallow conditions (7%) but ranged from 15–21% and from 24–26% of the applied N as KNO_3 and urea, respectively, in wheat-stubble fields. Nitrapyrin did not affect the immobilization of fertilizer N, and the amounts of fertilizer N recovered in the organic and in the inorganic N pools were similar in urea and urea plus nitrapyrin treatments 8 months after fertilizer application (Table XV).

Other studies have suggested an interesting pathway of nitrite incor-

Table XIV

Effect of ATC Nitrification Inhibitor on Decay of Microbial Biomass in Loam Soil in a 12-Week Laboratory Incubation[a]

Treatment	$^{15}NH_4$ released on fumigation and incubation (ng/g soil)	^{15}N in biomass (ng ^{15}N/g soil)	Decay rate constant[c]	$t_{1/2}$[d] (weeks)
NH_4OH 1[b]	18	60	0.028	24.7
NH_4OH 2[b]	14	47	0.026	27.2
NH_4OH plus ATC	38	127	0.020	33.9
Urea plus ATC	35	117	0.026	26.2

[a] From Juma and Paul (1983).

[b] Similar treatments incubated at separate times.

[c] Decay rate constant expressed as net decay/week, setting the initial pool sizes to 100%.

[d] Half-lives for biomass ^{15}N.

poration into the organic nitrogen fraction via nitrite self-decomposition and fixation on organic matter in a humic-rich acidic forest soil (pH, 4.5; organic matter, 46%) (Boudot and Chone, 1985). Nitrapyrin application not only reduced the loss of nitrite via chemodenitrification (Nelson, 1982) but also decreased the incorporation of nitrite into the organic N fraction (Boudot and Chone, 1985). In later studies, Azhar *et al.* (1986a) reported that nitrite formed from ammonium oxidation in grassland soil (pH, 6.5; organic C, 4.09%) was incorporated into the organic matter fraction following the pathway suggested by Boudot and Chone (1985). Nitrapyrin application checked the fixation of nitrite into organic matter. It is

Table XV

Recovery of Fall-Applied ^{15}N-Labeled Urea in May 1981 in the Soil Profile (kgN/ha) to 30-cm Depth of Baline Lake Clay Loam (Typic Udic Haploborolls)[a]

Treatment[b]	Organic N[c]	$(NH_4 + NO_2 + NO_3)$ N[c]	Fixed NH_4 N[c]	Total N[c]
Urea	12.2 a	32.4 a	0.7 a	45.3 b
	(24.4)[d]	(64.7)	(1.4)	(90.5)
Urea plus	14.5 a	32.7 a	1.2 b	48.3 b
nitrapyrin	(28.9)	(65.3)	(2.3)	(96.6)

[a] From Aulakh and Rennie (1984).

[b] Urea was applied at the rate of 50 kg N/ha and nitrapyrin at a concentration of 1% of active ingredient per weight of fertilizer N on 27 September 1980.

[c] In each column, the values differ significantly ($p < 0.05$) when not followed by the same letter.

[d] Values in parentheses represent the percentage recovery of fertilizer N.

important to note that this mechanism of nitrite fixation in organic matter has been reported in soils in which nitrification occurred and nitrite accumulated only in small amounts (Azhar *et al.*, 1986b,c). It has been proposed that nitrite formed reacted with phenols, forming nitro- and nitrosophenols. Nitrosophenols tautomerized to form quinone oxime, which could be reduced or oxidized chemically or enzymatically ultimately to form gaseous products of nitrogen. Results from these studies suggest an interesting pathway such that nitrification could lead to incorporation of mineral N ($N0_2$) into organic N. Nitrapyrin has been found to block this pathway by checking NO_2 accumulation in soils.

It should be made clear here that nitrification inhibitors increase immobilization of N by increasing the persistence of NH_4. Also, nitrification inhibitors check NO_2 accumulation in soils and thus block fixation of NO_2 into organic matter. These two examples are simply two different aspects of the N immobilization process. Nitrite accumulation and its fixation into organic matter occurs under specific soil conditions (Chalk and Smith, 1983), whereas immobilization of mineral N is a more general process, but both are influenced by nitrification inhibitors.

B. DENITRIFICATION

It has been reported that nitrification inhibitors can inhibit denitrification is soils. For example, Mitsui *et al.* (1964) showed that nitrapyrin, dicyandiamide, and sodium azide retarded denitrification of nitrate N in wetland rice soils. Similarly, Henninger and Bollag (1976) found that sulfathiazole (ST), potassium azide, and phenylmercuric acetate (PMA) inhibited denitrification by soil microorganisms, but they could not confirm the inhibitory effect of nitrapyrin on denitirification. Other compounds, such as AM (2-amino-4-chloro- 6-methyl pyrimidine), ATC, and anilines also had no effect on denitrification. Some pesticides and nonspecific inhibitors of nitrification may also retard the denitrification process in soil (e.g., see Hauck, 1980, 1983; Goring and Laskowski, 1982). Yeomans and Bremner (1985a,b) found that none of the several herbicides, fungicides, and insecticides tested had any significant effect on denitrification of nitrate when added at 10 mg/kg soil concentration. Some of them had small effects when added at 50 mg/kg soil concentration. These results suggest that commonly used pesticides will have little effect on denitrification when added at normal rates.

McElhannon and Mills (1981) investigated the effect of nitrapyrin on denitrification of nitrate in a field planted to sweet corn in a 2-year study. It was found that nitrapyrin reduced the loss of nitrate by denitrification in situations in which a readily oxidizable carbon substrate was available, for example, in the rhizosphere of a living plant, and when nitrapyrin was applied to the nitrogen fertilizer band rather than by broadcast application. Contrary to these findings, Notton *et al.*, (1979) found that nitrapyrin stimulated denitrification of nitrate, particularly in the presence of carbon sources such as root debris or acetone in sand culture used for growing turnip, cauliflower, and radish plants.

Acetylene, which is an effective inhibitor of nitrification (Walter *et al.*, 1979; Sahrawat *et al.*, 1987), also inhibits nitrous oxide reductase enzyme, which converts N_2O to N_2 (Federova *et al.*, 1973; Yoshinari and Knowles, 1976; Yoshinari *et al.*, 1977), and, consequently, the gaseous product of denitrification is released largely as N_2O. In fact, the acetylene block technique is used to measure denitrification loss in soils by measuring N_2O emissions on a short-term basis (Yoshinari *et al.*, 1977; Ryden and Rolston, 1983; Keeney, 1986).

Bremner and Yeomans (1986) evaluated the effects of 28 nitrification inhibitors on denitrification of nitrate in soil by determining their influence on the amounts of nitrate lost and the amounts of nitrite, nitrous oxide (N_2O), and N_2 produced when soil samples were incubated anaerobically after treatment with nitrate. The inhibitors evaluated included nitrapyrin (N- Serve); etridiazole (Dwell); potassium azide; 2-amino-4-chloro-6-methyl pyrimidine; sulfathiazole (ST); 4-amino-1,2,4-triazole; 2,4-diamino-6-trichloromethyl-*s*-triazine; potassium ethylxanthate; sodium diethyldithiocarbamate; phenylmercuric acetate (PMA); caffeic acid; and dicyandiamide. It was found that only potassium azide of the nitrification inhibitors studied retarded denitrification of nitrate when added at the rate of 10 mg/kg soil. Some results of this study are given in Table XVI. When added at the rate of 50 mg/kg soil, only potassium azide and 2,4-diamino-6-trichloromethyl-*s*-triazine of the compounds tested inhibited denitrification. The other inhibitors either had no appreciable effect on denitrification or enhanced it when added at the rate of 10 or 50 mg/kg soil.

The inhibitory effects of nitrapyrin and etridiazole (Dwell) on denitrification reported earlier (Mitsui *et al.*, 1964; Mills and McElhannon, 1983, 1984; Mills *et al.*, 1976; McElhannon and Mills, 1981; Mills, 1984) could not be confirmed because these compounds had no effect on denitrification when added at the rate of 10 mg/kg soil and enhanced denitrification when they were added at the rate of 50 or 100 mg/kg soil (Bremner and Yeomans, 1986).

C. NITROUS OXIDE EMISSION VIA NITRIFICATION AND DENITRIFICATION

It is generally believed that nitrous oxide (N_2O) in soils is produced only through denitrification (CAST, 1976) but other research has clearly established that N_2O is also produced during nitrification of ammonium

Table XVI

Effects of Some Nitrification Inhibitors on Denitrification of Nitrate in Soil[a,b]

Nitrification inhibitor	NO_3 N lost (mg/kg soil)	N produced (mg/kg soil)		
		N_2O N	N_2 N	(NO_2 + N_2O + N_2) N
None	109	34	74	108
Nitrapyrin (N-serve)	109	36	72	108
Potassium azide	88	1	87	88
2-Amino-4-chloro-6-methyl pyrimidine (AM)	108	32	75	107
2-Mercaptobenzothiazole	110	38	72	110
Sulfathiazole (ST)	108	39	68	107
Etridiazole (Dwell)	109	33	75	108
Potassium ethylxanthate	107	26	81	107
Thiourea	109	35	74	109
4-Amino-1,2,4-triazole (ATC)	109	39	70	109
Sodium diethyldithiocarbamate	110	38	73	111
Phenylmercuric acetate (PMA)	116	20	78	117
Dicyandiamide (DCD)	108	39	69	108
2,4-Diamino-6-trichloromethyl-*s*-triazine (CL-1580)	108	31	76	107
Caffeic acid	109	33	74	107

[a] From Bremner and Yeomans (1986).

[b] Thirty-gram samples of Canisteo soil (Typic Haplaquoll) were incubated at 30°C with 15 ml water under He atmosphere after treatment with 9 mg nitrate N as KNO_3 and O.3 mg of the inhibitor (10 mg/kg soil) specified.

(Bremner and Blackmer, 1978; Freney *et al.*, 1978, 1979; Goodroad and Keeney, 1984; Aulakh *et al.*, 1984; Sahrawat *et al.*, 1985). The mechanism of N_2O production via nitrification is not clearly understood. The production of N_2O via denitrification of nitrate and nitrification of ammonium can be represented as follows:

$$NO_3 \xrightarrow{\text{Nitrate reductase}} NO_2 \xrightarrow{\text{Nitrite reductase}} N_2O \xrightarrow{\text{Nitrous oxide reductase}} N_2 \qquad (1)$$

$$\begin{tikzcd} NH_4 \arrow[r] & NH_2OH \arrow[r] & \text{Unidentified } (H_2N_2O_2?) \text{ compound} \arrow[r] \arrow[d] & NO_2 \arrow[r] & NO_3 \quad (2) \\ & & N_2O & & \end{tikzcd}$$

Because nitrification inhibitors retard oxidation of ammonium to nitrite, it is not surprising that they also retard N_2O emissions through nitrification of ammonium. Bremner and Blackmer (1978) showed that nitrapyrin greatly reduced emission of N_2O from soils during nitrification of ammonium (Table XVII). Acetylene (C_2H_2), which retards nitrification of ammonium, also greatly reduces emissions of N_2O from soils during nitrification of ammonium (Table XVIII) (Bremner and Blackmer, 1979; Aulakh *et al.*, 1984). Smith and Chalk (1978, 1980) studied the effect of nitrapyrin addition on evolution of N_2O, N_2, nitric oxide (NO), and nitrogen dioxide (NO_2) gases from a calcareous soil treated with ammonia. Nitrapyrin largely reduced the gaseous loss of N_2 and oxides of N including N_2O from soil. Nitrite accumulation occurred in soil treated with ammonia but was prevented by nitrapyrin (see Table X). It is recognized that nitrification inhibitors such as nitrapyrin check accumulation of nitrite N in soils and thus are likely to reduce N_2O emissions via chemodenitrification or microbial denitrification of nitrite N indirectly (e.g., see Bremner and Blackmer, 1980; Nelson, 1982; Hauck, 1983; Chalk and Smith, 1983). Freney *et al.* (1979) found that N_2O emitted from soils, apparently via nitrification, at water contents ranging from air-dry to field capacity was inhibited by $HgCl_2$ and toluene.

Field studies have shown that nitrapyrin added at field rates of application reduced N_2O emissions induced by fertilization of soils with urea and anhydrous ammonia (Table XIX) (Bremner *et al.* 1981; Aulakh *et al.*, 1984). In a field study of N_2O emission from Australian soils, it was found that under fallow conditions, nitrapyrin significantly reduced anhydrous ammonia-induced loss of N_2O only from a calcareous soil (pH, 8.5, organic C, 1.3%) but not from another soil (pH, 7.5; organic C, 2.0%). The inhibitor

Table XVII

Effect of Nitrapyrin on Emission of N_2O from a Clay Loam Soil (pH 7.8; organic C 4.4%) Incubated under Aerobic Conditions after Treatment with Different Forms of N[a,b]

Form of N added	Nitrapyrin added (μg/g soil)	Amount of N_2O N evolved in 20 days (μg/g soil)
None	0	4
None	8	4
Ammonium [$(NH_4)_2SO_4$]	0	148
Ammonium	8	10
Urea	0	122
Urea	8	4
Nitrate (KNO_3)	0	6
Nitrate	8	4

[a] From Bremner and Blackmer (1978).

[b] Different forms of N were added at a rate of 100 mg/kg soil and incubated at 60% WHC moisture and 30°C.

Table XVIII

Effects of Acetylene on Nitrification and N_2O Production in a Clay Loam Soil (pH 8.1, organic C 4.2%) Treated with Ammonium under Aerobic Conditions[a,b]

Treatment			
Ammonium added (μg/g soil)	C_2H_2 added (%, v/v)	(NO_2 + NO_3) N produced in 12 days (mg/kg soil)	N_2O N evolved in 12 days (ng/g soil)
0	0	11	—
0	0.1	<1	—
100	0	105	208
100	0.1	<1	<1

[a] From Bremner and Blackmer (1979).

[b] Soil samples (30 g) were treated with $(NH_4)_2SO_4$ and incubated at 100 cm water tension under air or air containing C_2H_2 (0.1%, v/v) at 30°C. Atmospheres in incubation vessels were renewed at 3-day interval.

had little effect on nitrification in the non-calcareous soil, probably due to its high content of organic matter (Magalhaes *et al.*, 1984).

In a laboratory study, Aulakh and Rennie (1985) found that potassium azide (KN_3), a nitrification inhibitor, caused a severalfold increase in N_2O emissions from soils under aerobic conditions when added at a rate of 1 m*M*. Nitrogen added either as NH_4 or NO_3 had no effect on azide-induced N_2O production (Table XX). Azide also inhibited nitrification, as reported

Table XIX

Effects of Nitrapyrin on N_2O Emission from Soil Fertilized with Anhydrous Ammonia[a,b]

Treatment	Amount of N_2O N evolved (kg N/ha) in 167 days	
	Fall application	Spring application
None	0.16	0.43
Anhydrous ammonia	1.55	1.37
Anhydrous ammonia plus nitrapyrin	1.04	0.55

[a] From Bremner *et al.* (1981).

[b] Anhydrous ammonia (180 kg N/ha) and nitrapyrin (0.56 kg/ha) were applied on 9 October 1979 for the fall application and on 15 April 1980 for the spring application.

Table XX

Effects of KN_3 on N_2O Emission and CO_2 Evolution in Elston Clay Loam during 96 Hours of Incubation[a,b]

N Source	KN_3[c]	N_2O N evolved[d] (μg/g soil)	CO_2 C evolved[d] (μg/g soil)
$(NH_4)_2SO_4$	−	84 ± 12 a	57 ± 9 a
	+	1121 ± 40 b	85 ± 4 b
KNO_3	−	20 ± 3 a	57 ± 9 a
	+	1674 ± 101 b	87 ± 6 b
KNO_2	−	3556 ± 247 a	131 ± 14 a
	+	1346 ± 646 b	111 ± 11 a

[a] From Aulakh and Rennie (1985).

[b] Soil samples (100 g) were treated with 50 μg N/g soil as $(NH_4)_2SO_4$, KNO_3, or KNO_2 with and without KN_3 (1 m*M*) and incubated at 60% moisture saturation at 25 ± 1°C for 96 hr.

[c] −, KN_3 not added; +, KN_3 added at 1 m*M* rate.

[d] The values in the same column within each source in the absence and presence of KN_3 are significantly different at $p < 0.05$ when not followed by the same letter.

previously. Addition of nitrapyrin or C_2H_2 to azide showed that they had no effect on azide-induced N_2O emissions. It was postulated that KN_3 stimulated denitrification by possibly enhancing the synthesis of denitrifying enzymes. Azide stimulated general microbial activity in soil treated with $(NH_4)_2SO_4$ and KNO_3, as measured by CO_2 evolution (Table XX).

Nitrapyrin has been found to have little direct effect, if any, on N_2O evolution through denitrification of nitrate N in soils, although it greatly reduces the production of N_2O via nitrification (e.g., see Bremner and Blackmer, 1980). A study by McElhannon and Mills (1981), however, showed that nitrapyrin reduced nitrate fertilizer-induced N_2O emissions from soil planted to sweet corn. Bremner and Yeomans (1986), however, could not confirm the effect of nitrapyrin on denitrification of nitrate in a laboratory study in which mineral N as well as gaseous products of denitrification were determined.

Casella *et al.* (1986) used 0.1% C_2H_2 (v/v) under aerobic and anaerobic conditions to determine N_2O production via nitrification of ammonium and denitrification of nitrate and concluded that N losses by denitrification may potentially be higher than those occurring via nitrification. Davidson *et al.* (1986) have developed a technique based on the effects of low and high concentrations on C_2H_2 on nitrification and denitrification for distinguishing between nitrification and denitrification as sources of nitrous oxide production in soils. The measurements of denitrification N_2O were made from 24-hr laboratory incubations in which nitrification was inhibited by 10 Pa C_2H_2. Nitrification N_2O was estimated from the differences between N_2O production in the absence of C_2H_2 and that determined for denitrification. Denitrification N_2O was estimated from the differences between N_2O production at 10 kPa C_2H_2 and that at 10 Pa C_2H_2.

It was found that the laboratory estimates of N_2O were significantly correlated with field measurements in two forested watersheds during a 10-month period. These authors suggested that this technique is suitable for distinguishing between N_2O production during nitrification and denitrification, which is important because the source of N_2O produced in soil is often uncertain due to the possibility that denitrification and nitrification can occur simultaneously in the soil. This technique may also be suitable for qualitative study of the environmental parameters that regulate gaseous N loss via nitrification and denitrification (Davidson and Swank, 1986).

There is an obvious need for further research to clarify the effects of nitrification inhibitors on N_2O production through denitrification of nitrate in the presence of growing plants.

D. UREA HYDROLYSIS

It has been generally found that the compounds proposed as nitrification inhibitors have little effect, if any, on urea hydrolysis when added at normal recommended rates (Mulvaney and Bremner, 1981). For example, Goring (1962b) found that nitrapyrin did not affect urea hydrolysis and was a specific inhibitor of the first step of the nitrification process, i.e., conversion of ammonium to nitrite. Similiarly, Bremner and Douglas (1971) Bundy and Bremner (1974), and Bremner and Bundy (1976) showed that of the several nitrification inhibitors tested (nitrapyrin, AM, ST, ATC, and several substituted anilines) for their effect on urea hydrolysis, only potassium azide (KN_3) retarded urea hydrolysis to some extent when applied at 10 or 50 μg/g soil rates. However, Reddy and Prasad (1975) reported that nitrapyrin (1% of urea N) retarded urea hydrolysis in soil. It was found that potent nitrification inhibitors such as carbon disulfide (CS_2) and sodium trithiocarbonate (Na_2CS_3), which release CS_2 upon decomposition, and nitrapyrin had little effect on urea hydrolysis in soil (Ashworth *et al.*, 1977). Studies have also shown that DCD, a nitrification inhibitor, does not affect urea hydrolysis in soil (Amberger and Vilsmeier, 1979; Hauck and Behnke, 1981; Rodgers, 1983). Guthrie and Bomke (1981) also showed that ATC and nitrapyrin had no effect on urea hydrolysis at 2 or 20 μg/g soil rates of application.

However, in other studies thiourea and ammonium thiosulfate were found to retard urea hydrolysis in addition to retarding nitrification in soils (Malhi and Nyborg, 1979a,b; Goos, 1985). Ammonium thiosulfate retarded urea hydrolysis in soils but did not affect urea hydrolysis by jackbean urease (Table XXI). Thiourea retarded urea hydrolysis in soil (Table XXII) at very high concentrations (urea:thiourea, 2:1). Such high rates of thiourea may unfavorably affect its practical use. It would appear that both thiourea and ammonium thiosulfate are general metabolic inhibitors rather than specific urease inhibitors (Goos, 1985). In an earlier study, Sahrawat (1979a) found that thiourea had a small effect on urea hydrolysis (10% inhibition) in a sandy clay loam soil when added at a 50 mg/kg rate.

Ashworth *et al.* (1979) showed that potassium ethylxanthate, a nitrification inhibitor, was also a moderately effective inhibitor of urease activity in soils. Further studies showed that xanthates of unsubstituted alcohols of low molecular weight were very effective inhibitors of nitrification in soil at 20°C when added at the rate of 20 mg/kg of soil. The xanthates were also found to retard urease activity in soils when added at 200 mg/kg of soil (a concentration 10 times higher than that used for inhibition of nitrification) (Ashworth *et al.*, 1980). However, the xanthates were comparatively less effective urease inhibitors than benzoquinone in Maywood clay loam (Mollic Cryoboralf, pH 6.2, organic matter 2.6%) (Table XXIII). The effectiveness of xanthates in retarding nitrification and urease activity was not well correlated with the amounts of carbon disulfide evolved from soil treated with xanthates in sealed chambers. Mishra *et*

Table XXI

Inhibitory Effect (%) of Ammonium Thiosulfate (ATS) on Urea Hydrolysis of Urea Ammonium Nitrate (UAN) by Soil Urease and Jackbean Urease[a]

	Amounts of ATS added to UAN (%, v/v)					
	0	1	2	5	10	SE[b]
	William loam soil[c]					
2 days	0 (20)[d]	20	28	45	50	5
4 days	0 (62)[d]	35	45	47	52	3
	Jackbean urease[e]					
1 hr	0 (75)[d]	0	0	0	0	—

[a] From Goos (1985).

[b] Standard error.

[c] Soil samples (25 g) were treated with aqueous solutions containing different volumes of UAN and ATS and incubated at 25°C for 2 or 4 days.

[d] Values in parentheses show the percentage of the original urea hydrolyzed in the control (no ATS added).

[e] THAM buffer containing jackbean urease was treated with different volumes of UAN and ATS and incubated at 25°C for 1 hr.

Table XXII

Effects of Formulation of Urea with Thiourea and Pellet Size on Its Hydrolysis in the Field on Malmo Silty Clay Loam (Black Chernozem)[a]

Treatment[b]	Pellet size (g)	Urea N hydrolyzed[c] at 8 days in 0–15-cm soil (apparent %)
Urea	0.01	98 a
Urea plus thiourea (2:1)	0.01	49 d
Urea	0.21	84 b
Urea plus thiourea (2:1)	0.21	36 e
Urea	2.26	63 c
Urea plus thiourea (2:1)	2.51	25 f

[a] From Malhi and Nyborg (1979a).

[b] Urea and thiourea were pelleted together and added at a rate of 112 kg N/ha considering N both in urea and thiourea. Urea plus thiourea was added at a rate of 178.5 kg urea and 89.2 kg of thiourea/ha.

[c] Values not followed by the same letter are significantly different ($p < 0.05$).

Table XXIII

Effects of Xanthates, Benzoquinone, and Sodium Trithiocarbonate on Urease Activity in a Clay Loam Soil[a,b]

Compound	Inhibition of urease activity after 24 hr (%)
Benzoquinone	82
Sodium trithiocarbonate	22
Potassium methyl xanthate	74
Sodium methoxymethyl xanthate	49
Potassium allyl xanthate	48
Potassium ethyl xanthate	29
Potassium 2-methoxyethyl xanthate	49
Potassium isopropoxyethyl xanthate	21
Potassium ethylene glycol xanthate	18
Potassium 2-dimethylaminomethyl xanthate	29
Sodium 2-nitrilo-2-propyl xanthate	19

[a] From Ashworth *et al.* (1980).

[b] Soil samples (18 g) were treated with 400 mg of urea N and 200 mg of the inhibitor per kilogram of soil and incubated at 15% water content under aerobic conditions at 23°C.

al. (1980) studied the effects of some quinoid and phenolic compounds on urease activity and found that 1,4-naphthoquinone; 2-methyl-1,4-napthoquinone; 2,3- dichlorohydroquinone; 4,6-di*tert*-butyl-*o*-benzoquinone; 4,6-di-*tert*-butylpyrocatechol; and 4-*tert*-butylpyrocatechol added at 10 and 20 mg/kg soil rates retarded urea hydrolysis to varying degrees in addition to retarding nitrification.

Some organophosphorus insecticides were also found to retard urea hydrolysis (e.g., see Lethbridge and Burns, 1976; Sahrawat, 1979b) in addition to retarding nitrification in soil (Sahrawat, 1980).

IV. OTHER EFFECTS

In addition to the effects of nitrification inhibitors discussed above, they may also affect soil-borne plant diseases (Huber and Watson, 1974; Huber *et al.*, 1977; White *et al.*, 1978) and growth of leguminous and cereal crops due to phytotoxicity (for review see Sahrawat and Keeney, 1984). It has been found that in general nitrapyrin and 6-CPA were more phytotoxic to dicotyledenous plants than to grasses (Geronimo *et al.*, 1973a,b). Nitrapyrin has also been found to be toxic to leguminous plants, such as soybean and alfalfa (McKell and Whalley, 1964; Riley and Barber, 1970), and to cotton and ryegrass (Parr *et al.*, 1971). The effects of nitrification inhibitors on plant disease, phytotoxicity, and plant quality and composition were discussed by Sahrawat and Keeney (1984).

Janzen and Bettany (1986) studied the effect of ammonium thiosulfate on nitrification of ammonium in Weyburn loam soil (Typic Cryoborolls; pH, 7.2; organic C, 2.8%) It was found that unlike nitrification inhibitors such as nitrapyrin, thiosulfate inhibited the second step of nitrification, the oxidation of nitrite to nitrate, and resulted in the accumulation of high concentrations (as high as 42 mg NO_2 N/kg soil) of nitrite N. The accumulation of nitrite was very conspicuous at higher concentrations of thiosulfate.

The accumulation of nitrite may thus pose a serious drawback in the use of ammonium thiosulfate as a nitrification inhibitor, because it is known that small nitrite concentrations, as low as 2 mg N/kg can adversely affect plant growth (Keeney, 1982). Additionally, thiosulfate has been reported to be toxic to plants (Audus and Quastel, 1947) and may also retard other beneficial microbial processes (Schmidt, 1982).

The inhibitory effect of thiosulfate on soil nitrification may be due to the toxic effect of thiosulfate or its oxidation products, tetrathionate and sulfite, on *Nitrobacter,* resulting in slowed nitrate formation (Janzen and Bettany, 1986). It is also possible that the effect on ammonium oxidation they have little, if any, direct effect on denitrification and associated N_2O production. There is an urgent need to develop chemicals that can control N_2O production in soils associated with both nitrification and denitrification. Better understanding of the enzyme system involved in N_2O production via processes of nitrogen transformations should aid in developing chemicals that could block the specific enzyme system that is responsible for N_2O production (Sahrawat and Keeney, 1986). The best way, of course, of reducing N_2O emissions from soils is by increasing the efficiency of N in crop production.

It should be emphasized that the retardation of nitrification affects the microsite chemistry of soils by increasing the persistence of ammonium, with a concomitant rise in soil pH. These two changes greatly affect the subsequent nitrogen transformations such as ammonium fixation, ammonia volatilization, immobilization, and N_2O production in soils. High soil pH at the microsite level may also greatly affect the solubilization of organic matter, and this could change the course of the release of mineral nitrogen and other plant nutrients. It is very important to follow the changes in soil pH, particularly at the microsite level, in studies investigating the effects of nitrification inhibitors on nitrogen transformation processes in relation to soil physical and chemical characteristics.

There is an obvious need to generate information as to how the microsite soil pH changes brought on by retardation of nitrification affect the physical, chemical, and biological processes relevant to nitrogen transformations in soils. The more important processes that are likely to be influenced and have relevance to nitrogen cycling in soils and its availability to plant, are obviously nitrogen mineralization, immobilization, and remineralization and ammonium fixation; these should receive research priority. It is hoped that this review will stimulate research on the varied effects of nitrification inhibitors on nitrogen transformations in soil. This area of research should develop in importance with the increasing interest in the use of nitrification inhibitors.

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