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Thiophosphoryl triamide: a dual purpose urease/nitrification inhibitor

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Abstract

Very few compounds have been shown to possess both urease and nitrification inhibitor activity. The ability to control both of these processes by the addition of a single additive is, however, highly desirable. During our work with the urease inhibitor thiophosphoryl triamide (TPTA) we have discovered that this material affects inhibition of urea hydrolysis by urease and ammonium oxidation by nitrifiers. This discovery suggests the pursuit of a new class of agrochemical compounds which can be designated as ammonium/nitrate ratio control agents because of their potential ability to provide controllable levels of ammonium and nitrate to cropping systems.

Introduction

Loss of fertilizer nitrogen from agricultural cropland is a worldwide problem. Of the three primary plant nutrients (nitrogen, phosphorus, and potassium), nitrogen is used in the largest quantities and with the least efficiency. It is estimated that worldwide only about 50% of the applied fertilizer nitrogen is recovered by cereal crops [1]. This loss of fertilizer nitrogen represents both an economic loss and a pollution source. In the United States alone it is estimated that the annual loss of fertilizer nitrogen represents an economic loss of 700 million dollars [8], and nitrate pollution of groundwater from the agricultural usage of fertilizer is an area of growing concern.

About half of the nitrogen not utilized by crops is immobilized as soil inorganic nitrogen; the other half is lost via one or both of three quite different reaction sequences which occur after nitrogen-containing fertilizer is added to the soil.

The first sequence of reactions which occurs with urea-based fertilizers is the urease catalyzed hydrolysis of urea to ammonia.

The ammonia produced then reacts with soil water to provide ammonium cation.

This sequence serves a vital function in providing inorganic nitrogen for growing plants. However, the urease-induced hydrolysis of urea is very rapid, and this can cause a buildup of free ammonia in the soil microsite around the fertilizer; and considerable loss of ammonia by volatilization often occurs [13].

The second reaction sequence is the biological oxidation of ammonium to nitrite and nitrate by nitrosomonas and nitrobacter bacteria. This reaction sequence results with ammonia-based fertilizers such as ammonium nitrate and ultimately with urea-based fertilizers after they are converted to ammonium forms.

This process, known as nitrification, can lead to nitrogen losses by leaching and denitrification. In the United States, it has been reported that approximately 25% of the applied fertilizer nitrogen is lost by leaching and denitrification [10].

Urease and nitrification inhibitors can delay the urease catalyzed hydrolysis of urea and the nitrification of ammonium nitrogen respectively. In agricultural systems where such losses are potentially high, the use of these materials would provide increased nitrogen efficiencies and reduced pollution.

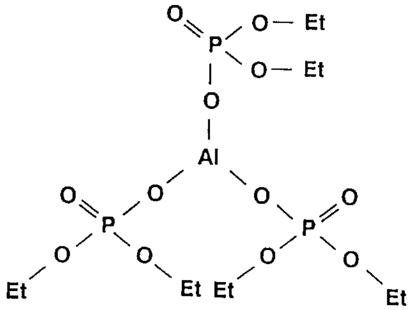
Urease inhibitors. Although a wide variety of chemicals have been shown to inhibit urease activity, none have yet been commercialized. Phenyl phosphorodiamidate (PPDA), $(C_6H_5O)PO(NH_2)_2$, has probably been the most widely studied urease inhibitor in recent years and until recently was considered the best known inhibitor. Two relatively new inhibitors, thiophosphoryl triamide (TPTA), $(NH_2)_3PS$ [14], and N-(n-butyl)-thiophosphoryl triamide (NBTPTA), $[NH(CH_3CH_2CH_2CH_2)]\text{-}(NH_2)_2PS$ [11], are currently receiving considerable attention in terms of commercial development. Both of these compounds have been shown to give superior inhibition to PPDA. The Tennessee Valley Authority has been granted a statutory invention registration on TPTA SIR No. H25 [14] and a patent on the use of TPTA in fluid fertilizers [8]. The inhibitor NBTPTA was patented by Allied Corporation in 1985 [11].

Even though urease has been extensively studied for about 60 years and a large number of compounds have been identified as urease inhibitors and nitrification inhibitors, until now no urease inhibitors have been reported which are similarly effective as nitrification inhibitors.

Nitrification inhibitors. Although a large number of many different types of compounds have been found to inhibit nitrification (many of which are patented), only seven have been recently produced commercially for use as nitrification inhibitors. Four of these [2-amino-4-chloro-6-methyl pyridine (AM), 2-mercaptobenzothiazole (MBT), sulfathiazole (ST), and thiourea (TU)] are produced and marketed primarily in Japan.

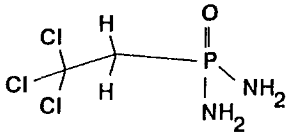
Controlling ammonium/nitrate nutrition with urea-based fertilizers may require both urease inhibitors (to control the ammonium levels and prevent ammonia toxicity) and nitrification inhibitors (to extend the availability of ammonium in the soil) and more preferably a compound or substance which will perform both roles.

Dual action inhibitors. An intensive search of the literature has revealed only two instances in which phosphorus-containing compounds have shown nitrification inhibition properties. U.S. Patent 4,315,762 [6] describes the use of aluminium tris(O-ethyl phosphonate) I. These materials have a covalent aluminum-phosphorus bond and are of the formula:

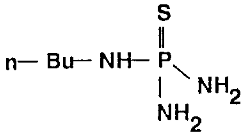


I

The second instance describes the results of a series of tests on nine phosphoroamides which were found effective as urease inhibitors [4]. Of the nine phosphoroamides tested only two exhibited minimal inhibitory activity, the trichloroethyl phosphorodiamidate (II) and n-butyl-phosphorothioic triamide (III). These phosphoroamides have the structures shown below.



II



III

This later compound appeared to inhibit nitrification only at very high rates of application (10 to 20 times), and to a much lower extent (25–33%) when compared with nitrapyrin or etridiazole (both commercial inhibitors) in terms of inhibitor-to-soil ratios and incubated at 20°C. When the incubation temperature is raised to 30°C, the inhibition is even lower (4–12%).

There is little consensus concerning optimum ammonium/nitrate ratios for crop growth. This is not surprising since the ammonium/nitrate ratio available to roots affects physiological processes by a number of mechanisms. This area of concern was recently reviewed by Bock [2].

Relatively little is known about the optimum ratios necessary for maximum crop yields. Recent studies have shown, however, that high ammonium/nitrate ratios during early plant growth can result in decreased yields [3]. In a field study using urea and dicyandiamide (DCD), ratios as high as 31:1, within 11 days of planting, i.e., during at least a portion of the germination stage, significantly reduced yields at harvest (by about 10%) even though ratios remained high during the remaining portion of the growing season.

Although no studies have documented the exact ratios needed for optimum plant growth and yield, it is postulated that high ammonium/nitrate ratios during the reproduction, or in the case of grain crops, during the grain-filling stage, are necessary for maximum yields [2].

Experimental

Materials. Thiophosphoryl triamide and NBTPTA were synthesized by the method of Goehring and Niedenzu [9] and purified by column chromatography. Urea, DCD, and ammonium sulfate were obtained commercially and used with no further purification.

Nitrification inhibitor testing method. Thiophosphoryl triamide was tested for nitrification inhibition using the soil testing procedure described below.

Mountview silt loam soil was screened through a 2-mm sieve. Plexiglas containers (8 × 8 × 6 cm) were packed half-full with the soil and packed to a bulk density of $1.0\,g/cm^2$ and wetted to field capacity (approximately 20 weight percent moisture). The ammonium sulfate (887 mg per container which supplied N equal to that of 410 mg urea) and inhibitor (41 mg per container at the 10% level, urea basis) were added in a narrow band, i.e., about 0.5 cm, and additional soil was added to fill the containers. The total amount of dry soil added was 384 g. The containers were incubated at 25°C. During incubation, the containers were checked periodically for moisture loss and water added as needed to maintain moisture levels.

The individual containers were removed from the incubator at 1-, 2-, 3, 4-, and 5-week intervals. After removal from the incubator, the contents of the containers were transferred to plastic bags and thoroughly mixed. A 10-g sample of soil (dry basis) was taken from each bag and extracted with 100 mL of 2 N KCl. The extract was filtered through a Whatman No. 41 filter paper and refrigerated until analyzed. Samples were analyzed for NO_3-N and NO_2-N using a colorimetric procedure. The samples were also analyzed for NH_4-N. In each test situation, two replicates were utilized to obtain the average values.

The percent nitrification inhibition was calculated according to the method of Bundy and Bremner [5]:

$$\%\ \text{nitrification inhibition} = [(C - S)/C] \times 100 \quad (4)$$

where C = net amount of NO_3-N produced in the control (no inhibitor added) and S = net amount of NO_3-N produced in the inhibitor treated sample.

Ammonium/nitrate ratio control testing method. Thiophosphoryl triamide was tested as a dual-purpose nitrification inhibitor/urease inhibitor using the testing procedure described above with the following modifications. Urea was used as the nitrogen source, and the KCl extract was analyzed for urea using a colorimetric procedure.

Results and discussion

Thiophosphoryl triamide as a nitrification inhibitor. Thiophosphoryl triamide was tested for its ability to inhibit nitrification in soils by the nitrification inhibitor testing method as described above. Dicyandiamide was added for comparison as a nitrification inhibitor and NBTPTA for comparison as another candidate dual purpose inhibitor. The results (Table 1) showed that nitrification inhibition obtained with TPTA was less than that obtained with DCD but significantly greater than that obtained with NBTPTA, and remained at about the 50% level after 5 weeks.

The data in Table 1 show that significant levels of ammonium remain for TPTA at the 5-week

Table 1. Nitrification inhibition tests with TPTA and NBTPTA as ammonium/nitrate control agents with ammonium sulfate as N-source-5-weeks' incubation

Inhibitor	NO_3-N, mg	% inhibition	NH_4-N, mg	NO_3-N + NH_4-N, mg	% N recovered
1 week					
None	18.0	0.0	145.9	163.9	86.9
DCD, 41.0 mg	3.1	82.8	155.9	159.0	84.3
TPTA, 41.0 mg	3.8	78.9	166.7	170.5	90.4
NBTPTA, 41.0 mg	16.5	8.3	145.2	161.7	85.7
2 weeks					
None	122.5	0.0	62.6	185.1	98.5
DCD, 41.0 mg	4.6	96.2	149.8	154.4	82.1
TPTA, 41.0 mg	23.0	81.2	138.6	161.6	86.0
NBTPTA, 41.0 mg	110.2	10.0	63.4	173.6	92.3
3 weeks					
None	122.5	0.0	14.2	136.7	72.5
DCD, 41.0 mg	5.8	95.3	150.1	155.9	82.7
TPTA, 41.0 mg	73.7	39.8	108.7	182.4	96.7
NBTPTA, 41.0 mg	147.5	−20.4	25.3	172.8	91.6
4 weeks					
None	179.3	0.0	4.6	183.9	97.8
DCD, 41.0 mg	5.8	96.8	160.1	165.9	88.2
TPTA, 41.0 mg	99.5	44.5	85.6	185.1	98.5
NBTPTA, 41.0 mg	163.6	8.8	13.4	177.0	94.2
5 weeks					
None	180.5	0.0	1.2	181.7	96.7
DCD, 41.0 mg	5.0	97.2	157.8	162.8	86.6
TPTA, 41.0 mg	84.5	53.2	100.2	184.7	98.2
NBTPTA, 41.0 mg	172.0	4.7	1.9	173.9	92.5

sampling time while no ammonium is present for the NBTPTA, thus confirming the nitrification inhibition effect of TPTA and the inability of NBTPTA to inhibit nitrification. These data clearly show that TPTA is an effective nitrification inhibitor in soil systems.

Thiophosphoryl triamide as an ammonium/nitrate ratio control agent. Thiophosphoryl triamide was tested for its ability to control the ratio of ammonium to nitrate with urea-based fertilizers by the ammonium/nitrate ratio control testing method as described above. The inhibitor DCD and urea without inhibitor were tested for comparison. The results given in Table 2 show that even after 5 weeks' incubation at 25°C, 99.6% apparent nitrification inhibition was obtained with TPTA compared with 90% inhibition for the DCD treatment, 80% inhibition for the NPTPTA treatment, and 0% for the urea without inhibitor.

It should be noted that the apparent nitrification inhibition for TPTA and NBTPTA is a result of both nitrification and urease inhibition for TPTA only. Note also that with TPTA initial levels of ammonium are low, which will help in preventing seedling damage, while ammonium values rise throughout the 5-week period, providing continually increasing ammonium/nitrate ratios. The NBTPTA, on the other hand, provides only urease inhibition and extends low levels of ammonium past the 5-week period.

Table 2 shows the ammonium/nitrate nutrition ratios (as calculated from the data of Table 2) for DCD, TPTA, and NBTPTA. Note that DCD shows a high ammonium/nitrate ratio (78:1) at the 1-week interval, which could be detrimental to seedling germination, plant development, and crop yield. The ratio then remains relatively stable between 5:1 and 7:1. On the other hand, TPTA shows a gradually increasing ammonium/nitrate ratio and peaks at the 4-week interval. This confirms the fact that in addition to maintaining appropriate levels of ammonium during the 5-week period, the ammonium/nitrate ratio remained at a higher level.

Table 2. Nitrification inhibition tests with TPTA and NBTPTA as ammonium/nitrate control agents with urea as N-source-5-weeks' incubation

Inhibitor	NO_3-N, mg	% inhibition	NH_4-N, mg	Urea-N, mg	Total NO_3 + NH_4 + urea-N, mg	% N recovered	Ratio NH_4:NO_3
				1 week			
None	21.0	0.0	107.9		129	68.4	5.0:1
DCD	1.0[a]	4.6	78.2	117.2	195.2	104.0	78.2:1
TPTA	3.1	85.3	21.5	182.4	207	109.8	7.0:1
NBTPTA	5.4	74.4	18.5	192	215.9	114.5	3.4:1
				2 weeks			
None	155.5	0.0	30.8		186.3	98.8	0.2:1
DCD	17.7	88.6	134.2		151.9	80.5	7.8:1
TPTA	3.8	97.6	46.5	159.40	209.7	111.2	12.10:1
NBTPTA	11.1	92.9	5.8	197.80	214.7	113.3	0.5:1
				3 weeks			
None	180.1	0.0	2.3		182.3	96.6	.01:1
DCD	22.7	87.4	130.0		148.4	78.7	5.7:1
TPTA	3.8	97.9	70.1	111.40	186.5	98.9	18.2:1
NBTPTA	13.8	92.3	5.8	195.90	215.5	114.3	0.42:1
				4 weeks			
None	180.5	0.0	0.0		180.5	95.7	–
DCD	22.7	87.4	126.6		149.3	79.2	5.7:1
TPTA	1.0[a]	100.0	106.8	70.10	176.9	93.8	106:1
NBTPTA	24.2	86.6	5.9	186.30	216.4	114.7	0.24:1
				5 weeks			
None	184.7	0.0	0.6		185.3	98.3	–
DCD	18.4	90.0	131.6		150	79.5	7.2:1
TPTA	5.0	97.3	141.0		146	77.4	28.2:1
NBTPTA	28.4	84.6	4.4	172.80	205.6	109.1	0.15:1

[a] In both cases, no nitrate was detected, and 1 mg was assumed to be present to allow calculation of the ammonium/nitrate ratio. This number was not included in the total nitrogen recovery.

Conclusions

It is clear that although a large number of compounds have been identified and are patented separately as urease inhibitors or as nitrification inhibitors, there is no single inhibitor which meets all the needs of American agriculture. This paper reports the potential use of TPTA as a dual purpose urease/nitrification inhibitor. By virtue of these multiple inhibition characteristics, TPTA may be suitable for the control of urease hydrolysis, nitrification of ammonium to nitrate, and of a new characteristic of controlling and maintaining relative levels of ammonia and nitrate in the soil which are necessary for the proper ammonium/nitrate nutrition of agricultural crops. A great deal more research is needed to determine if such chemicals can be effectively used in various cropping systems. It is to be expected that other compounds can be found which exhibit similar but variable properties, depending on the specific compound, and that such properties can be matched with the requirements of the specific cropping systems.

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