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# Greenhouse Study on the Effects of the Urease Inhibitors Phenyl Phosphorodiamidate and N-(n-butyl) Thiophosphoric Triamide on the Efficiency of Urea Applied to Flooded Rice*

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## 1 Summary - Zusammenfassung

Urea was split applied to transplanted rice in a greenhouse experiment with two-thirds applied as labeled $^{15}N$ urea at 15 days after transplanting (DAT) and one-third (not labeled) at 42 DAT to determine the effect of the urease inhibitors phenyl phosphorodiamidate (PPDA) and N-(n-butyl) thiophosphoric triamide (NBPT) on urea hydrolysis, plant uptake, yield, and loss of fertilizer N. An acidifying agent [$Al_2(SO_4)_3$] and an algicide were used to reduce the floodwater pH and thus slow the degradation of PPDA, keeping it effective for a longer period. Algicide addition extended the effectiveness of PPDA inhibition by about 2 days and increased plant uptake and grain yield significantly over that with urea use alone. $Al_2(SO_4)_3$ addition extended the effectiveness of PPDA only about 1 day, increased N uptake slightly, but failed to increase grain yield. NBPT effectively slowed urea hydrolysis, more than doubled plant uptake over that with urea alone, and increased grain yield by 38%. Percolation at 0.5 cm per day caused plant N uptake to increase by about 6% in all treatments but it was not essential for the inhibitors to have a beneficial effect. For the first split application, fertilizer losses of 50% from urea were decreased to about 10% by use of NBPT and to 28% with PPDA alone, and by combination of PPDA with the algicide losses were 22%.

### Gefäßversuch zur Wirkung der Ureaseinhibitoren Phenylphosphordiamid und N-(n-butyl) thiophosphortriamid auf die Harnstoffverwertung von Naßreis

Die Harnstoffdüngung erfolgte 15 (2/3) bzw. 42 (1/3) Tage nach dem Auspflanzen von Reis; zur 1. Gabe wurde $^{15}N$ markierter Harnstoff verabreicht, um die Wirkung der Ureasehemmstoffe Phenylphosphordiamid (PPDA) und N-(n-butyl) thiophosphortriamid (NBPT) auf Harnstoffhydrolyse, N-Aufnahme, Ertrag und Dünger-N-Verluste zu bestimmen. Um den pH-Wert des Stauwassers herabzusetzen und so den PPDA-Abbau zu verlangsamen (längere Wirkungsdauer), wurden $Al_2(SO_4)_3$ und ein Algizid eingesetzt. Letzteres verlängerte die Hemmwirkung des PPDA um etwa 2 Tage und erhöhte signifikant N-Entzüge und Kornerträge gegenüber Harnstoff allein. Der Zusatz von $Al_2(SO_4)_3$ verlängerte die PPDA-Wirkung nur um etwa einen Tag und erhöhte die N-Aufnahme geringfügig, nicht aber den Kornertrag. NBPT verzögerte die Harnstoffhydrolyse deutlich: die N-Aufnahme stieg um mehr als das Doppelte, der Kornertrag um 38% gegenüber Harnstoff allein. Eine Perkolation von 5 mm/Tag bewirkte eine Erhöhung der N-Aufnahme um etwa 6%, brachte aber in der Hemmstoffvariante keine bessere N-Ausnutzung als im Vergleichsglied. Die N-Verluste nach Harnstoffdüngung (1. N-Gabe) wurden durch NBPT, dem wirksamsten Ureasehemmstoff, von 50 auf etwa 10%, durch PPDA alleine auf 28%, in Kombination mit dem Algizid auf 22% verringert.

## 2 Introduction

Urea is widely applied to rice in Southeast Asia because of its cost, availability, and high N content (*Martinez* and *Diamond*, 1984). It is difficult to incorporate urea well in a flooded soil without motorized machinery because of urea's high water solubility. Therefore, many Asian farmers simply broadcast the urea into standing floodwater after the seedlings are established (*De Datta*, 1986). High urease activity at the flooded soil surface leads to rapid urea hydrolysis, high ammoniacal-N concentrations in the floodwater, and potentially high $NH_3$ volatilization losses when weather conditions facilitate the removal of $NH_3$ from the water-air interface (*Bouwmeester* and *Vlek*, 1981). The use of chemicals to decrease the urease activity of soils has been proposed as a way to decrease the amount of N lost by $NH_3$ volatilization.

Published research regarding the potential of urease inhibitors to slow urea hydrolysis in plant studies was practically nonexistent until East German researchers found that phenyl phosphorodiamidate (PPDA) is a powerful urease inhibitor that can be used to decrease $NH_3$ volatilization losses from small grain fertilization (*Heber* et al., 1979; *Kämpfe* et al., 1982). The compound was used in greenhouse studies with flooded rice (*Vlek* et al., 1980; *Byrnes* et al., 1983) and later in field studies (*Fillery* et al., 1986a;

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*Simpson* et al., 1985; *Castillo*, 1985). In these studies, the use of PPDA generally increased N uptake by the plants by about 15% but rarely increased grain yields. A yield advantage was found only when the inhibitor was used in delayed application (*Fillery* et al., 1986a) or under conditions that leached urea below the aerobic zone (*Simpson* et al., 1985).

Characteristically urease inhibition by PPDA ends abruptly, after which urea hydrolysis proceeds at a rate similar to that in the uninhibited system. Concentrations of ammoniacal-N have then developed in the floodwater (*Simpson* et al., 1985; *Fillery* et al., 1986a). This loss of inhibition is thought to be due to the instability of PPDA to base hydrolysis under the high-pH conditions of floodwater (*Austin* et al., 1984; *Byrnes* et al., in press).

The urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) has recently been found to be a powerful urease inhibitor, and it was used successfully to decrease N losses in field studies of upland crops when conditions were conducive to high $NH_3$ volatilization losses (*Schlegel* et al., 1986). In laboratory incubation studies, NBPT was found to be a longer lasting inhibitor than PPDA in a variety of upland soils (*Bremner* and *Chai*, 1986).

The potential of urease inhibitors to decrease $NH_3$ volatilization and increase grain yield has not been fully tested because an effective, long-lasting inhibitor was not available.

This study was conducted to attempt to make PPDA effective for a longer period by decreasing the floodwater pH and to test the effectiveness of the inhibitor NBPT in a delayed application to flooded rice. Under conditions conducive to $NH_3$ volatilization, the inhibitors were tested for their ability to reduce the urea hydrolysis rate, decrease ammoniacal-N concentrations in the floodwater, and increase $^{15}N$ fertilizer uptake and grain yield.

## 3 Materials and Methods

The trial was carried out in Kick-Brauckmann pots (an inner bottomless pot which fits loosely into an exterior, larger pot).

### 3.1 Soil

Fresh moist silt loam (brown earth from loess). pH: 6.5, $N_t$: 1.2 g $kg^{-1}$, 7.22 kg dry weight/pot. The soil was flooded for 3 weeks, then fertilized with 0.43 g P [$Ca(H_2PO_4)_2 \cdot H_2O$] and 1.00 g K and 0.22 g S ($K_2SO_4$)/pot, incorporated in the top 8 cm of soil.

### 3.2 Crop

IR-36 rice (*Oryza sativa* L.)--a high-yielding, short-statured variety, widely adopted in Southeast Asia. Two 25-day-old transplants/pot.

### 3.3 Treatments

a. Control, no nitrogen
b. Urea alone, no inhibitor
c. Urea with PPDA
d. Urea with PPDA plus Cu-chelate
e. Urea with PPDA plus $Al_2(SO_4)_3$
f. Urea with PPDA plus $Al_2(SO_4)_3$ and Cu-chelate
g. Urea with NBPT
h. Urea with NBPT plus Cu-chelate

Each treatment either without percolation or with percolation of 5 mm/day. 3 replicates.

### 3.4 Rates of Additions

*3.4.1 N-Applications:* 300 mg N as $^{15}N$-labeled urea (46.703 g $kg^{-1}$ $^{15}N$ atom excess) to floodwaater 15 days after transplanting (DAT). 100 mg N as unlabeled urea at 42 DAT.

*3.4.2 Urease Inhibitors:* 13 mg/pot = 20 g $kg^{-1}$ of the weight of urea.

*3.4.3 Acidifying Agents:* 1 mg $kg^{-1}$ Cu added as Cu-chelate to floodwater 2 d before N fertilization (commercial algicide, 90 g $kg^{-1}$ Cu solution, tradename Cutrine Plus, from Applied Biochemists, Inc., Mequon, Wisconsin, U.S.A.). 0.1 g/pot $Al_2(SO_4)_3 \cdot 16\ H_2O$, this initially lowered the daytime pH of the floodwater to about 6.

### 3.5 Percolation and Management

75 mL of water was removed from between the outer and inner pots twice each day at 08.00 and 17.00 and placed directly into the floodwater (water level outside was 5 cm below the floodwater; after 6 h the levels were the same) for 20 d after the first fertilizer addition; with this system, there was no potential for loss of the $^{15}N$ fertilizer from the system through leaching. During this period, six 35-cm-diameter electric fans produced a gentle air movement (0.5-1.0 m $sec^{-1}$, depending on the distance of the pot from the fans) between 08.00 and 20.00. The pots were randomized weekly. Floodwater maintained at 3 cm depth.

### 3.6 Harvests

*3.6.1 First:* 42 DAT to measure $^{15}N$ uptake and dry-matter yield, at approximately maximum tillering. Before harvest, the water level was maintained in the pots at just below the soil surface.

*3.6.2 Second:* At maturity, 119 DAT. Because of the long day length in Germany, the plants did not progress from the vegetative to reproductive phase, so they were placed in the dark under a tent from 17.00 until 07.00 (July 11-August 9). One week before harvest the soil was allowed to dry.

The grain was threshed; unfilled grain and chaff were combined with the straw.

### 3.7 Analyses

*3.7.1 Floodwater:* 2 mL samples removed daily for urea (*Mulvaney* and *Bremner*, 1979) and ammoniacal-N (*Keeney* and *Nelson*, 1982) measured for 20 d following fertilization. pH with glass combination electrode every afternoon for 10 d following fertilization.

*3.7.2 Plant Materials:* Samples were dried at 60°C, ground to less than 1 mm and analyzed for total N and $^{15}N$ content (*Buresh* et al., 1982). The $^{15}N$ content was determined with a Micromass Model 622 mass spectrometer.

*3.7.3 Soil:* Soil from each pot was rapidly air-dried and major roots were separated, dried, ground (<1 mm), and then combined and mixed with ground soil. Total N (*Stumpe* et al., 1985) and $^{15}N$ content as with plant materials.

# 4 Results and Discussion

## 4.1 Effects on Floodwater Parameters

The urea-N concentration decreased rapidly in the unleached treatments when no inhibitor was added; only about one-fourth of the added urea remained in the floodwater one day after addition (Figure 1). Urease inhibition by PPDA improved by addition of $Al_2(SO_4)_3$ and by addition of the algicide. There was no significant difference in the rate of urea disappearance between the algicide with PPDA and the combination of $Al_2(SO_4)_3$ with the algicide (data not shown). The slowest decrease in urea concentration was achieved by NBPT, and urea remained in the floodwater for up to 2 weeks. There was no difference in the urea disappearance when NBPT was used with the algicide compared with NBPT by itself (data not shown). The characteristic inflection point at which PPDA failed to further inhibit the urease was not evident in this study as it was in others (*Byrnes* et al., 1983; *Vlek* et al., 1980) possibly because the urea was being transported rapidly into the soil due to high water use by the plants.

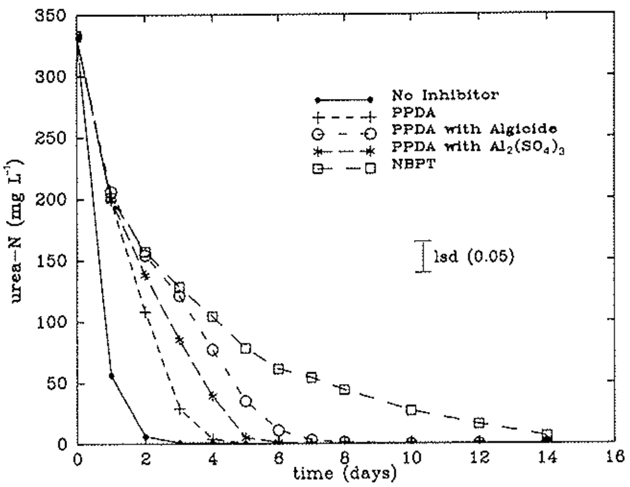


**Figure 1:** Concentrations of Urea-N in the Floodwater with Time as Effected by Inhibitor and Acidifying Agents.
**Abbildung 1:** Veränderung der Harnstoffgehalte des überstauten Wassers in Abhängigkeit von Hemmstoffen und versauernden Substanzen.

The pH of the control was very high, nearly 10.0 on sunny days and 9.3-9.5 on overcast days (Table 1). With urea alone the pH was 8.4-8.7 the first three days, then rose to about 10.0 after $NH_3$ volatilization was completed.

With the high pH of the PPDA treatment, base hydrolysis of PPDA would be rapid (*Austin* et al., 1984). Addition of algicide caused the daytime pH to be one pH unit lower on the first day compared with PPDA use alone (Table 1), but it then rose to 10.0 on the fourth day after fertilization. The lower daytime pH was maintained more effectively by algicide addition than by $Al_2(SO_4)_3$ alone. Even though the pH reductions were not great, they increased the length of inhibition by PPDA. The treatment with NBPT and no algicide had high pH values, which were reduced about one-half pH unit by algicide addition. The treatment with PPDA had a lower pH on days 3 and 4 (Table 1) when the urea hydrolysis occurred and ammoniacal-N developed in the floodwater (Figure 2).

**Table 1:** Average Daytime pH of the Floodwaters
**Tabelle 1:** Mittlere tägliche pH-Werte des überstauten Wassers

| Treatment | Days After Fertilization 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| | (pH) | | | | |
| No urea | 9.8 | 9.9 | 9.5 | 10.0 | 9.9 |
| Urea alone | 8.7 | 8.4 | 8.6 | 9.9 | 10.0 |
| PPDA | 9.8 | 9.7 | 8.8 | 8.8 | 9.4 |
| PPDA, Cu-chelate | 8.8 | 9.1 | 8.9 | 10.0 | 9.8 |
| PPDA, $Al_2(SO_4)_3$ | 9.3 | 9.5 | 8.5 | 9.4 | 9.2 |
| PPDA, $Al_2(SO_4)_3$, Cu-chelate | 8.8 | 9.3 | 9.0 | 10.0 | 9.7 |
| NBPT | 9.6 | 9.8 | 9.1 | 10.0 | 9.9 |
| NBPT, Cu-chelate | 8.9 | 9.1 | 8.6 | 9.6 | 9.4 |
| | S[a)] | S | O | S | S |
| lsd (0.05 level) = 0.3 | | | | | |

a) S indicates sunny conditions, and O indicates overcast conditions.

Rapid urea hydrolysis produced very high concentrations of ammoniacal-N on the first day when no inhibitor was used (Figure 2). Urease activity was extremely high due to biological activity promoted by the abundance of nutrients, water, and light at the soil surface. The peak concentration of ammoniacal-N decreased rapidly, presumably because of rapid $NH_3$ volatilization. Addition of PPDA decreased the peak concentration of ammoniacal-N to about one-half that of the uninhibited treatment, and $Al_2(SO_4)_3$ or algicide reduced it further.

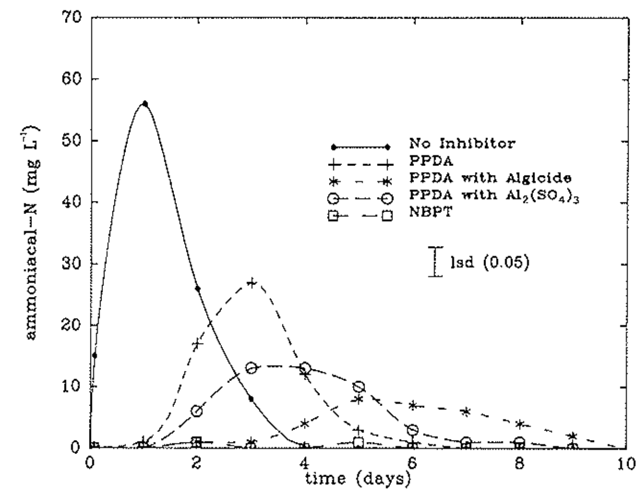


**Figure 2:** Concentrations of Ammoniacal-N in the Floodwater with Time as Effected by Inhibitor and Acidifying Agents.
**Abbildung 2:** Veränderung der Ammoniumgehalte des überstauten Wassers in Abhängigkeit von Hemmstoffen und versauernden Substanzen.

While the peak ammoniacal-N concentrations were reduced by progressively better inhibition, they were present for longer periods with the slowed urea hydrolysis. The ammoniacal-N concentrations with NBPT were 1 mg $L^{-1}$ N or less throughout the 20 d following fertilization. Thus, urea disappeared from the floodwater mainly by movement into the soil, and urea hydrolysis was so slow that adsorption and immobilization by algae allowed no accumulation of ammoniacal-N in the floodwater. There was no significant difference in ammoniacal-N concentrations between the PPDA treatments with the algicide and combination of the algicide and $Al_2(SO_4)_3$ (data not shown). Reduced floodwater pH decreased PPDA degradation, which extended its inhibitory effectiveness and reduced the ammoniacal-N accumulation.

## 4.2 Nitrogen Recovery

Water percolation of 5 mm $d^{-1}$ through the soil increased the $^{15}N$ recovery by the plants at 42 DAT by 7.2% on average and by 4.4% in the grain at maturity (Table 2). The recovery in the straw and soil were not significantly (0.05 level) affected by percolation. Plant recovery of added N was uniformly increased by percolation across the N treatments, and thus there was no N treatment by leaching interaction. Therefore, the average $^{15}N$ recoveries for the leached and unleached treatments are discussed.

**Table 2:** Effect of Percolation on the $^{15}N$ Fertilizer Recovery in the Plants and Soils at the Two Harvests

**Tabelle 2:** Wirkung der Perkolation auf die Wiederfindungsrate des Dünger-$^{15}N$ in Pflanzen und Boden zu den zwei Erntezeitpunkten

| Harvest and Fraction | Average $^{15}N$ Recovery Without Percolation | With Percolation | Significance[a)] |
|---|---|---|---|
| | % | | |
| 42 DAT harvest, plant | 47.5 | 54.7 | * |
| Maturity, straw | 19.8 | 20.7 | NS |
| Maturity, grain | 31.9 | 36.3 | * |
| Maturity, soil | 23.8 | 23.9 | NS |
| Total recovery at maturity | 75.5 | 81.0 | * |

a) * = significant at a 5% level by Duncan's multiple range test; NS = not significant at a 5% level.

Plant recoveries at 42 DAT were in all cases greater with the inhibitors than with urea by itself (Table 3): increases were from 11.1% of the fertilizer with PPDA alone to about 35% for NBPT. Addition of the algicide with PPDA caused 16.0% more uptake than with PPDA alone. Addition of $Al_2(SO_4)_3$ significantly increased early plant uptake, by 6.2% over PPDA alone.

For the maturity harvest, there was a wider range in the grain recoveries than in the straw recoveries. The grain recoveries showed practically the same relationships as those at the early harvest. There were no significant differences in the $^{15}N$ uptake of the straw as a result of any of the acidifying additions, while it was increased by NBPT. Just about all of the fertilizer $^{15}N$ had entered the plant by the early harvest, and total $^{15}N$ recovery in the straw plus the grain ranged from only 1.8% less to 7.3% more at maturity than at the early harvest. The recoveries of $^{15}N$ in the soil at maturity ranged from 20.4% to 26.9%. Practically the only significant difference in fertilizer recovery in the soil was that urea by itself had less recovery than any of the inhibited treatments.

Total $^{15}N$ recoveries were increased by 19.1% to 42.1% of the added fertilizer by addition of urease inhibitors. Algicide addition significantly increased total recovery over that with PPDA use alone, by 6.9% both with and without $Al_2(SO_4)_3$. Use of $Al_2(SO_4)_3$ did not preserve more $^{15}N$ than with PPDA alone, apparently due to the peak accumulation of ammoniacal-N being higher with PPDA by itself, but the concentration with the addition of $Al_2(SO_4)_3$ lasted about twice as long (Figure 2).

Loss of N from urea alone was 49.9%, which agrees with $NH_3$ volatilization losses found in other greenhouse studies under conditions which enhance losses (*Vlek* and *Craswell*, 1981), and in field studies under fairly high wind conditions (*Fillery* et al., 1986b). Although this loss is expected to be principally from $NH_3$ volatilization, the loss of 7.8% to 9.6% with the NBPT is likely through denitrification, since there was essentially no $NH_3$ in the floodwater to volatilize. This finding does not support the position that N saved from $NH_3$ volatilization would be largely lost by denitrification when $NH_3$ loss is eliminated (*Fillery* and *Vlek*, 1986), although eligibility of the N for denitrification loss is obviously increased by its preservation from volatilization

**Table 3:** Recoveries of $^{15}N$ Fertilizer at 42 DAT and at Maturity

**Tabelle 3:** Wiederfindungsrate des Dünger-$^{15}N$ 42 Tage nach dem Pflanzen und zur Kornreife

| Treatment | 42 DAT Plant | Maturity Harvest Straw | Grain | Soil | Total |
|---|---|---|---|---|---|
| | % | | | | |
| Urea alone | 26.9 E | 13.2 C | 16.5 D | 20.4 C | 50.1 E |
| PPDA | 38.0 D | 18.3 B | 27.0 C | 26.9 A | 72.2 CD |
| PPDA, Cu-chelate | 54.0 B | 21.1 B | 32.9 B | 25.1 AB | 79.1 B |
| PPDA, $Al_2(SO_4)_3$ | 44.2 C | 20.8 B | 23.0 C | 25.4 AB | 69.2 D |
| PPDA, $Al_2(SO_4)_3$, Cu Chelate | 54.7 B | 19.0 B | 33.9 B | 23.3 B | 76.1 BC |
| NBPT | 60.5 A | 25.6 A | 40.0 A | 24.9 AB | 90.4 A |
| NBPT, Cu-chelate | 63.8 A | 26.6 A | 40.8 A | 24.8 AB | 92.2 A |

Note: Numbers followed by the same letter are not significantly different at a 5% level by Duncan's multiple range test.

## 4 Results and Discussion

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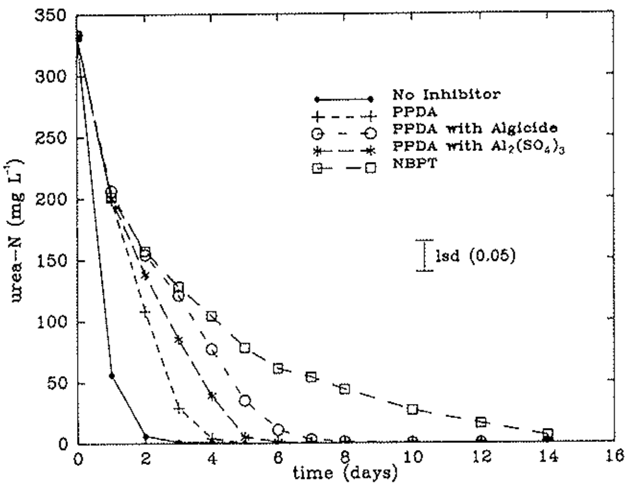


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| PPDA, Cu-chelate | 8.8 | 9.1 | 8.9 | 10.0 | 9.8 |
| PPDA, $Al_2(SO_4)_3$ | 9.3 | 9.5 | 8.5 | 9.4 | 9.2 |
| PPDA, $Al_2(SO_4)_3$, Cu-chelate | 8.8 | 9.3 | 9.0 | 10.0 | 9.7 |
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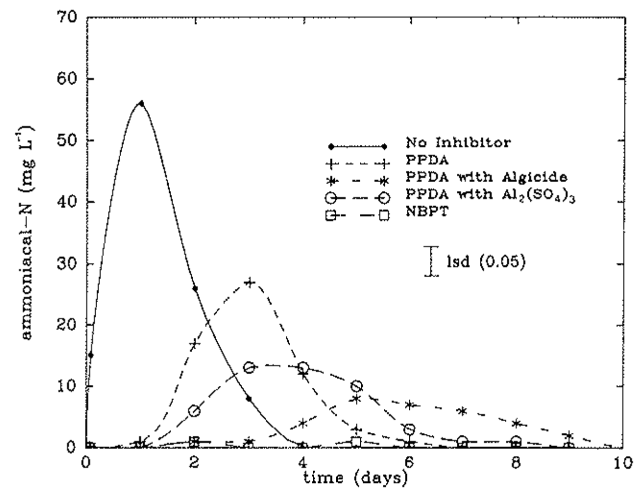
| | S[a)] | S | O | S | S |
| lsd (0.05 level) = 0.3 | | | | | |

a) S indicates sunny conditions, and O indicates overcast conditions.

Rapid urea hydrolysis produced very high concentrations of ammoniacal-N on the first day when no inhibitor was used (Figure 2). Urease activity was extremely high due to biological activity promoted by the abundance of nutrients, water, and light at the soil surface. The peak concentration of ammoniacal-N decreased rapidly, presumably because of rapid $NH_3$ volatilization. Addition of PPDA decreased the peak concentration of ammoniacal-N to about one-half that of the uninhibited treatment, and $Al_2(SO_4)_3$ or algicide reduced it further.

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(*Byrnes* and *Amberger*, in press). Also percolation did not have an interactive effect with inhibitor use, which would be expected if denitrification was a major loss mechanism.

### 4.3 Crop Yield

Water percolation did not have a significant effect on the rice yield at 42 DAT or at maturity (Table 4). The yield data were therefore averaged across the leaching treatments. There was a significant yield increase at both harvests due to N addition. Addition of PPDA by itself did not increase any of the yields significantly (0.05 level) over urea without an inhibitor, a finding in agreement with other results (*Castillo*, 1985; *Byrnes* et al., 1983; *Fillery* et al., 1986a).

**Table 4:** Yield of Rice as Affected by the Addition of Urease Inhibitors and Agents to Reduce the Floodwater pH

**Tabelle 4:** Wirkung von Ureaseinhibitoren und versauernden Substanzen auf den Reisertrag

| Treatment | 42 DAT | Maturity Harvest Straw | Maturity Harvest Grain |
|---|---|---|---|
| | (g/pot) | | |
| Control | 13.8 D[a)] | 36.3 B | 25.4 D |
| Urea alone | 18.7 C | 55.4 A | 34.8 C |
| PPDA | 20.3 BC | 58.9 A | 40.4 ABC |
| PPDA + algicide | 22.2 A | 56.1 A | 47.3 A |
| PPDA + $Al_2(SO_4)_3$ | 21.6 AB | 54.8 A | 37.9 BC |
| PPDA + $Al_2(SO_4)_3$ + algicide | 22.4 A | 53.6 A | 45.9 AB |
| NBPT | 23.3 A | 61.8 A | 48.6 A |
| NBPT + algicide | 23.5 A | 63.0 A | 47.4 A |
| Percolation | NS[b)] | NS | NS |
| Treatment | ** | ** | ** |
| Treatment x percolation | NS | NS | NS |

a) Numbers followed by the same letter are not significantly different at a 5% level by Duncan's multiple range test.
b) NS = not significant; ** = significant at 1% level.

For the early harvest, higher yields were produced by PPDA use with the acidifying agents and NBPT than by urea alone. PPDA used with an algicide produced a higher yield than did PPDA by itself, while addition of $Al_2(SO_4)_3$ did not increase grain yield over PPDA alone.

At maturity, straw yields were greatly increased by N addition, but there were no significant differences in straw yields between any of the N-fertilizer treatments. The high straw-to-grain weight ratio is probably due to the excessive vegetative growth due to the long day length.

The addition of PPDA to urea significantly increased grain yields over those with urea alone only if the algicide was used to help extend the effectiveness of the PPDA (Table 4); and $Al_2(SO_4)_3$ addition did not increase grain yield over urea alone. Addition of NBPT increased grain yield by an average of 38% over urea use by itself. The NBPT yields were not significantly greater than those for most of the PPDA treatments.

## 5 Conclusions

Addition of urease inhibitors and the use of substances to reduce the floodwater pH to maintain PPDA inhibition reduced urea hydrolysis rates and ammoniacal-N production, and increased $^{15}N$ recovery by the plants; these differences were reflected in yield. The acidifying substance used to reduce the floodwater pH was not very effective since this is a difficult system to buffer. Yet the slight and short-term reductions in pH were enough to significantly slow PPDA decomposition and prolong its effectiveness. The algicide was more successful at reducing the pH than $Al_2(SO_4)_3$ addition; however, the algicide had no effect when NBPT was used. This indicates that the primary effects of the algicide when used with PPDA, were on the stability of PPDA rather than N transformations due to biological processes (*Byrnes* et al., in press).

The effective inhibitor NBPT decreased fertilizer losses to less than 10% and increased the grain yield by 38% over that with urea alone. This demonstrates that under conditions conducive to $NH_3$ volatilization losses, effective urease inhibition can increase the efficiency of urea. Total recovery of $^{15}N$ with NBPT was similar to recoveries found with deep placement of urea (*Vlek* and *Craswell*, 1981). Differences in fertilizer uptake by the plants had to be 21% or more of the N applied in the first split before a significant difference in yield was found.

Soil percolation at a moderate rate had a constant effect of increasing the N efficiency on all N treatments by moving the N out of the area where $NH_3$ volatilization and nitrification- denitrification occur. This study does not indicate that soil percolation to reduce denitrification losses is necessary for an effective urease inhibitor to have a beneficial result with a delayed N application.

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## Acknowledgments

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## References

*Austin, E.R., T.J. Bradford*, and *M.S. Lupin* (1984): High-Performance Liquid Chromatographic Determination and Hydrolysis Studies of Phenyl Phosphorodiamidate, a Urease Inhibitor. J. Agr. and Food Chem. 32, 1090-1096.

*Bouwmeester, R.J.B.*, and *P.L.G. Vlek* (1981): Rate Control of Ammonia Volatilization From Rice Paddies. Atmos. Environ. 15, 131-140.

*Bremner, J.M.*, and *H.S. Chai* (1986): Evaluation of N-Butyl Phosphorothioic Triamide for Retardation of Urea Hydrolysis in Soils. Commun. in Soil Sci. Plant Anal. 17, 337-351.

*Buresh, R.J.*, *E.R. Austin*, and *E.T. Craswell* (1982): Analytical Methods in $^{15}N$ Research. Fert. Res. 3, 37-62.

*Byrnes, B.H.*, and *A. Amberger* (In press): Fate of Broadcast Urea in a Flooded Soil When Treated With N-(n-butyl) Thiophosphoric Triamide, a Urease Inhibitor. Fert. Res.

*Byrnes, B.H.*, *N.K. Savant*, and *E.T. Craswell* (1983): Effect of a Urease Inhibitor Phenyl Phosphorodiamidate (PPD) on the Efficiency of Urea Applied to Rice. Soil Sci. Soc. Am. J. 47, 270-274.

*Byrnes, B.H.*, *K. Vilsmeier*, *E.R. Austin*, and *A. Amberger* (In press): The Degradation of the Urease Inhibitor Phenyl Phosphorodiamidate (PPDA) in Solutions and Floodwaters. J. Agr. and Food Chem.

*Castillo, E.G.* (1985): M.S. Thesis, University of the Philippines.

*De Datta, S.K.* (1986): Improving Nitrogen Fertilizer Efficiency in Lowland Rice in Tropical Asia. Fert. Res. 9, 171-186.

*Fillery, I.R.P.*, and *P.L.G. Vlek* (1986): Reappraisal of the Significance of Ammonia Volatilization as an N Loss Mechanism in Flooded Rice Fields. Fert. Res. 9, 79-98.

*Fillery, I.R.P.*, *S.K. De Datta*, and *E.T. Craswell* (1986a): Effect of Phenyl Phosphorodiamidate on the Fate of Urea Applied to Wetland Rice Fields. Fert. Res. 9, 251-263.

*Fillery, I.R.P.*, *J.R. Simpson*, and *S.K. De Datta* (1986b): Contribution of Ammonia Volatilization to Total Nitrogen Loss After Applications of Urea to Wetland Rice Fields. Fert. Res. 8, 193-202.

*Heber, R.*, *S. Müller*, *W. Matzel*, and *H. Ansorge* (1979): Ammoniakverluste bei Harnstoffdüngung 4. Mitteilung: Einfluß des Ureasehemmers Phosphorsäurephenylesterdiamid auf die Höhe der $NH_3$-Verluste und die Düngewirkung des Harnstoffs in Modell- und Gefäßversuchen. Arch. Acker- u. Pflanzenbau u. Bodenkd. 23, 231-240.

*Kämpfe, K.*, *E. Linke*, *L. Herold*, *H.J. Hartbrich*, and *D. Torner* (1982): Ergebnisse der Prüfung von PPDA-Harnstoff unter natürlichen und simulierten Witterungsbedingungen in Mikroparzellen-Versuchen. Arch. Acker- u. Pflanzenbau u. Bodenkd. 26, 483-490.

*Keeney, D.R.*, and *D.W. Nelson* (1982): Nitrogen - Inorganic Forms, in *A.L. Page*, *R.H. Miller*, and *D.R. Keeney*: Methods of Soil Analysis, Part 2, American Society of Agronomy, Madison, Wisconsin, p. 643-693.

*Martinez, A.*, and *R.B. Diamond* (1984): Nitrogen Use in World Crop Production, in *R. Hauck*: Nitrogen in Crop Production. American Society of Agronomy, Madison, Wisconsin, p. 3-21.

*Mulvaney, R.L.*, and *J.M. Bremner* (1979): A Modified Diacetyl Monoxime Method for Colorimetric Determination of Urea in Soil Extracts. Commun. in Soil Sci. Plant Anal. 10, 1163-1170.

*Schlegel, A.J.*, *D.W. Nelson*, and *L.E. Sommers* (1986): Field Evaluation of Urease Inhibitors for Corn Production. Agron. J. 78, 1007-1012.

*Simpson, J.R.*, *J.R. Freney*, *W.A. Muirhead*, and *R. Leuning* (1985): Effects of Phenylphosphorodiamidate and Dicyandiamide on Nitrogen Loss From Flooded Rice. Soil Sci. Soc. Am. J. 49, 1426- 1431.

*Stumpe, J.M.*, *C.B. Christianson*, and *R.J. Buresh* (1985): An Aluminum Block Digestion Procedure for Determination of Total N in Soils Containing $^{15}N$. Commun. in Soil Sci. Plant Anal. 16, 1-14.

*Vlek, P.L.G.*, and *E.T. Craswell* (1981): Ammonia Volatilization From Flooded Soils. Fert. Res. 2, 227-245.

*Vlek, P.L.G.*, *J.M. Stumpe*, and *B.H. Byrnes* (1980): Urease Activity and Inhibition in Flooded Soil Systems. Fert. Res. 1, 191-202. [P4593P]

(*Byrnes* and *Amberger*, in press). Also percolation did not have an interactive effect with inhibitor use, which would be expected if denitrification was a major loss mechanism.

### 4.3 Crop Yield

Water percolation did not have a significant effect on the rice yield at 42 DAT or at maturity (Table 4). The yield data were therefore averaged across the leaching treatments. There was a significant yield increase at both harvests due to N addition. Addition of PPDA by itself did not increase any of the yields significantly (0.05 level) over urea without an inhibitor, a finding in agreement with other results (*Castillo*, 1985; *Byrnes* et al., 1983; *Fillery* et al., 1986a).

**Table 4:** Yield of Rice as Affected by the Addition of Urease Inhibitors and Agents to Reduce the Floodwater pH
**Tabelle 4:** Wirkung von Ureaseinhibitoren und versauernden Substanzen auf den Reisertrag

| Treatment | 42 DAT | Maturity Harvest Straw | Maturity Harvest Grain |
|---|---|---|---|
| | (g/pot) | | |
| Control | 13.8 D[a] | 36.3 B | 25.4 D |
| Urea alone | 18.7 C | 55.4 A | 34.8 C |
| PPDA | 20.3 BC | 58.9 A | 40.4 ABC |
| PPDA + algicide | 22.2 A | 56.1 A | 47.3 A |
| PPDA + $Al_2(SO_4)_3$ | 21.6 AB | 54.8 A | 37.9 BC |
| PPDA + $Al_2(SO_4)_3$ + algicide | 22.4 A | 53.6 A | 45.9 AB |
| NBPT | 23.3 A | 61.8 A | 48.6 A |
| NBPT + algicide | 23.5 A | 63.0 A | 47.4 A |
| Percolation | NS[b] | NS | NS |
| Treatment | ** | ** | ** |
| Treatment x percolation | NS | NS | NS |

a) Numbers followed by the same letter are not significantly different at a 5% level by Duncan's multiple range test.
b) NS = not significant; ** = significant at 1% level.

For the early harvest, higher yields were produced by PPDA use with the acidifying agents and NBPT than by urea alone. PPDA used with an algicide produced a higher yield than did PPDA by itself, while addition of $Al_2(SO_4)_3$ did not increase grain yield over PPDA alone.

At maturity, straw yields were greatly increased by N addition, but there were no significant differences in straw yields between any of the N-fertilizer treatments. The high straw-to-grain weight ratio is probably due to the excessive vegetative growth due to the long day length.

The addition of PPDA to urea significantly increased grain yields over those with urea alone only if the algicide was used to help extend the effectiveness of the PPDA (Table 4); and $Al_2(SO_4)_3$ addition did not increase grain yield over urea alone. Addition of NBPT increased grain yield by an average of 38% over urea use by itself. The NBPT yields were not significantly greater than those for most of the PPDA treatments.

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