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Movement of urea and its hydrolysis products as influenced by moisture content and urease inhibitors

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Abstract A laboratory experiment was conducted on an Aquic Udifluvent Belgian soil in order to study the movement of urea and its hydrolysis products. This study was carried out at two moisture levels (10 and 20%) upon the addition of three types of urease inhibitors: hydroquinone, phenylphosphorodiamidate (PPDA), and *N*-(n-butyl)phosphorothioic triamide (NBPT). The results clearly show the effects of the inhibitors in retarding the hydrolysis of urea. The highest effect was observed with NBPT, followed by hydroquinone, and PPDA. The effect was more pronounced at 10% than at 20% moisture content. It was clear that subsequent nitrification of the NH_4^+ formed was inhibited at the lower moisture level. At 10% moisture, from the 7th day of incubation on, some NH_4^+ moved about 3 cm and reached the top of the soil column. At 20% moisture, no NH_4^+ reached the surface as it was quickly nitrified. After 17 days of incubation and at 20% moisture, the total mineral N was more or less homogeneously distributed within the soil column. In contrast, at 10% moisture, the remaining urea and the hydrolysis products were still concentrated at the place of application. The distribution of urea and its hydrolysis products was comparable with 7 days of incubation at 20% moisture and 17 days at 10%.

Key words Urea · Urease inhibitors · Hydroquinone · Phenylphosphorodiamidate · *N*-(n-butyl)phosphorothioic triamide · Nitrification · Nitrogen movement

Introduction

Urea is a major source of N fertilizer for both upland crops and wetland rice (Stumpe et al. 1984; Bouwmeester et al. 1985; Gould et al. 1986). In most arable soils, urea is rapidly hydrolysed to NH_3 and CO_2 by soil urease activity. This can result in significant N losses through NH_3 volatilization as soil pH rises. It results in low fertilizer recoveries (Beyrouty et al. 1988; Christianson et al. 1990). The application of urease inhibitors slows down the hydrolysis and can improve the efficiency of urea as a fertilizer. PPDA has proved to be more effective in retarding urease activity under anaerobic conditions, while NBPT exceeds PPDA in the ability to delay urea hydrolysis in aerobic conditions (Wang Zhengping et al. 1991). According to Beyrouty et al. (1988) and Watson (1990), PPDA is more effective in acid than in alkaline conditions, while NBPT is active in both conditions. Due to the lower cost of hydroquinone and its effects on some other soil N-transformation processes, this compound has also attracted research attention (Yeomans and Bremner 1986; Wang Zhengping et al. 1990).

Not only the use of urease inhibitors but also a subsurface application can improve the urea fertilizer efficiency (Gould et al. 1986). Once hydrolysed, NH_3 can be further nitrified. There are conflicting data on the influence of urease inhibitors on nitrification (Bundy and Bremner 1974; Bremner and Chai 1989; Wang Zhengping et al. 1990). The rate of the nitrification process depends considerably on pH and moisture content.

The objective of the present study was to investigate the movement of urea and its hydrolysis products in soil cores at different moisture contents when the urea was applied with or without urease inhibitors.

Materials and methods

Soil and urease inhibitors

The soil used was a surface Aquic Udifluvent Belgian soil, sampled at a depth of 0–20 cm after a wheat-growing season before any fertilizer was applied. After sampling, it was air-dried and crushed to pass a 1-mm screen. The main soil characteristics are shown in Table 1.

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Table 1 Physical and chemical characteristics of the soil used (*CEC* cation exchange capacity)

pH-H_2O	Particle size			Organic matter (%)	Total N (%)	C:N	$CaCO_3$ (%)	CEC (cmol kg^{-1})
	0–2 μm (%)	2–50 μm (%)	>50 μm (%)					
8.16	17.80	37.30	44.90	2.46	0.13	10.98	5.17	16.1

Three urease inhibitors were evaluated in this study: hydroquinone, provided by UCB Co., Belgium; PPDA and NBPT, provided by Enichem Americas, NJ, USA.

Procedure

In order to restore microbial activity, the soil was pre-incubated at 25°C and at a moisture content of 10 and 20% for 5 days. Thereafter, the soil was packed into a plastic cylinder of 10 cm height and 9.5 cm diameter. Two levels of moisture content were investigated: 10% and 20%, on a soil dry weight basis. The density of the packed soil core was 1.5 g cm^{-3}. The water evaporated during the pre-incubation was assessed by weighing the soil before and after incubation.

The three urease inhibitors were applied together with urea (300 mg urea-N per kg of soil) 3–4 cm below the surface of the packed soil column, mixed with the soil at that depth. A treatment without inhibitors (control) was also applied. The inhibitor concentration was 1% of the urea applied. The cores were then incubated at 25°C.

After 2, 4, 7, 12, and 17 days, the soil cores were sliced into 10 sections, each 1 cm thick. Part of the soil sample was used for moisture determination, and part was used for extraction with 1 *M* KCl. The remaining urea N in each section was determined by the modified diacetyl monoxime method (Mulvaney and Bremner 1979). NH_4^+-N and (NO_2+NO_3)-N were determined by distillation in the presence of MgO and Devarda's alloy (Bremner 1965).

Results and discussion

Influence of different urease inhibitors on urea-N movement at 10% moisture content

Table 2 shows that in the treatment without inhibitors, 75% of the added urea was not hydrolysed within 2 days of incubation. During this period, the applied urea-N

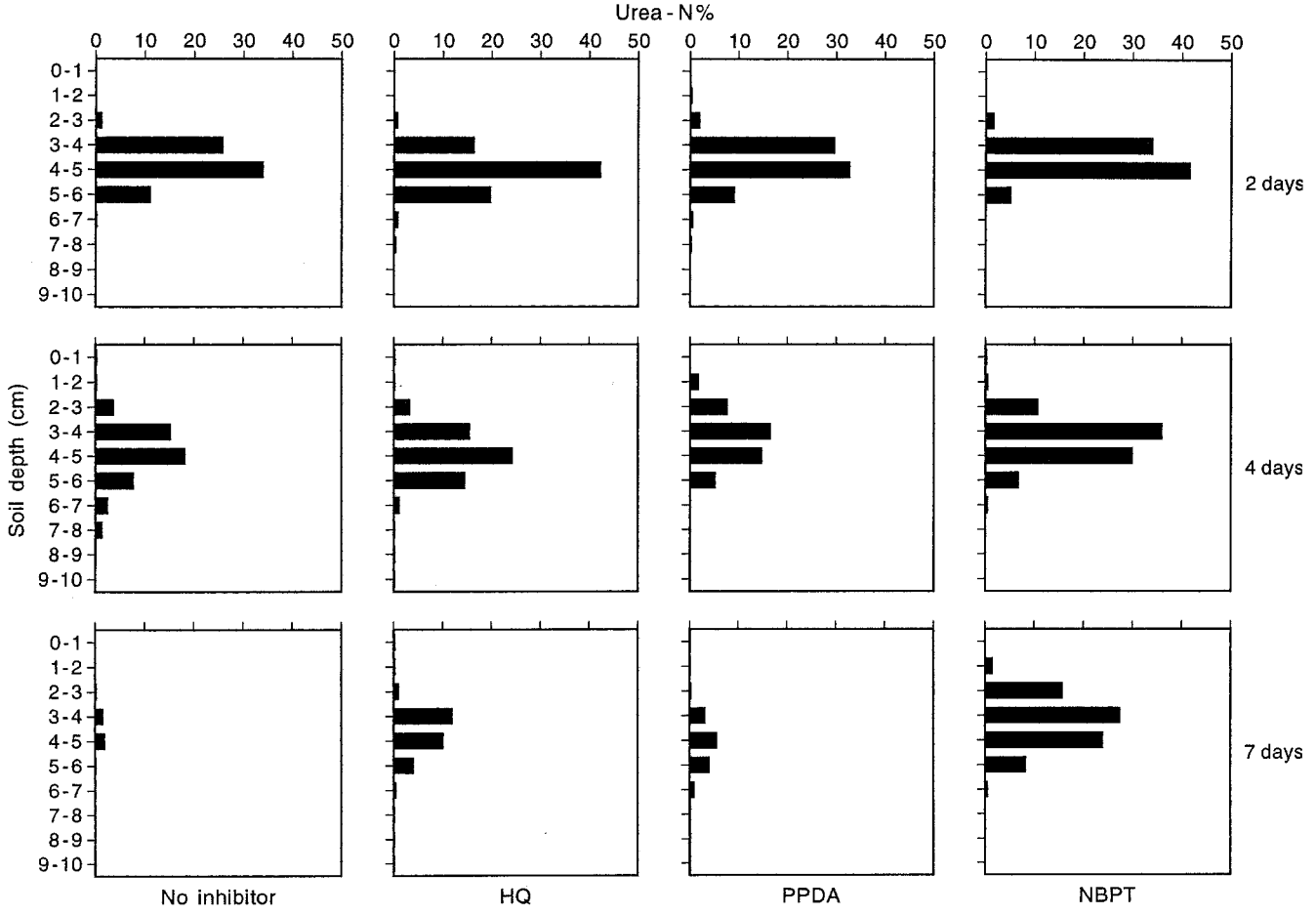

Fig. 1 Effect of urease inhibitors on urea-N movement at 10% moisture content, expressed as a percentage of the added urea N. The percentage indicated relates to a 1-cm layer of soil

Table 2 Recovery of urea N as a percentage of the urea N applied in the total soil column at 10% moisture content. *HO* hydroquinone, *PPDA* phenylphosphorodiamidate, *NBPT* *N*-(n-butyl)phosphorothioic triamide

Inhibitor	Time (h)				
	2	4	7	12	17
None	75	50	5	0	0
HQ	79	61	30	5	2
PPDA	75	47	15	2	2
NBPT	84	83	77	54	13

spread both up and down from a depth of 3–4 cm into a depth of 2–7th cm as shown in Fig. 1. After 4 days, about half the applied urea was hydrolysed and the rest was distributed over a depth of 1–8 cm. After 7 days, the hydrolysis of the urea was nearly completed. Diffusion and hydrolysis occurred simultaneously, so that the applied urea both spread out and decreased. At the same time, NH_4^+-N accumulated, followed by formation of NO_2^--N and NO_3^--N.

The addition of hydroquinone slightly slowed down the urea hydrolysis. After 2 and 4 days of incubation, 79 and 61% of the applied urea-N remained in the soil core, respectively. After 7 days, 30% of the applied urea was still not hydrolysed. As shown in Table 2, the urea remaining was six times that in the control soil. More urea-N moved into the deeper layers in the hydroquinone treated soil core than in the control. After 2 days of incubation, 61% of the applied urea was diffused into a depth of 4–6 cm (Fig. 1). It was clear that the inhibition of urea hydrolysis by hydroquinone allowed more urea to diffuse before hydrolysis.

PPDA did not show a clear inhibitory effect during the first 4 days compared to experiments in which PPDA was homogeneously mixed with the soil (Wang Zhengping et al. 1991). This might have been a result of a faster degradation of PPDA at the higher soil pH created by the larger amount of applied urea (Byrnes 1988). After 7 days of incubation, a slight inhibitory effect by PPDA was observed compared to the control (Table 2). This might have been due to a decomposition product of PPDA, which also has an inhibitory effect on urea hydrolysis (Hendrickson and O'Connor 1987).

The inhibition with NBPT was much stronger than with hydroquinone and PPDA. After 2 days of incubation, 84% of the applied urea was recovered in the soil and most of it was distributed over a depth of 3–5 cm (Table 2, Fig. 1). After 4 days, almost the same amount of urea-N was found in the soil core. About 77% of the applied urea remained at 2–6 cm even after 7 days of incubation. The

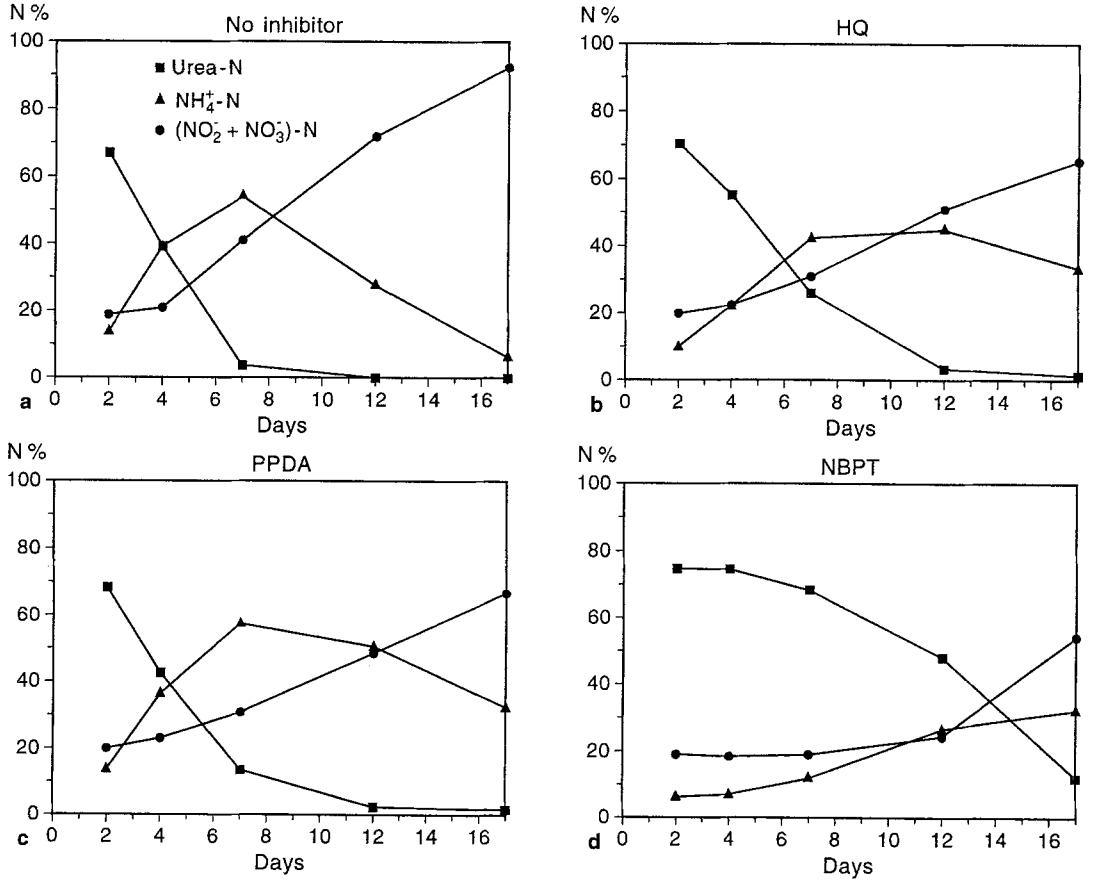

Fig. 2 Percentage distribution of different N compounds as influenced by urease inhibitors at 10% moisture content (*HQ* hydroquinone, *PPDA* phenylphosphorodiamide, *NBPT* *N*-(n-butyl) phosphorothioic triamide)

urea did not diffuse below 6 cm. The soil water level might have an important influence.

Since urea hydrolysis was strongly affected by the addition of different urease inhibitors, the NH_4^+-N accumulation was also pronouncedly influenced. In the control (Fig. 2a) and the less strongly inhibited (PPDA) treatment (Fig. 2c), more NH_4^+-N accumulated after 2 days and this became more significant after days 4 and 7. This accumulated NH_4^+-N was distributed over a depth of 1–7 cm (Fig. 3). After 7 days, the accumulated NH_4^+-N reached the maximum concentration in the control and PPDA treatment. About 55–57% of the total urea-N plus mineral N was in

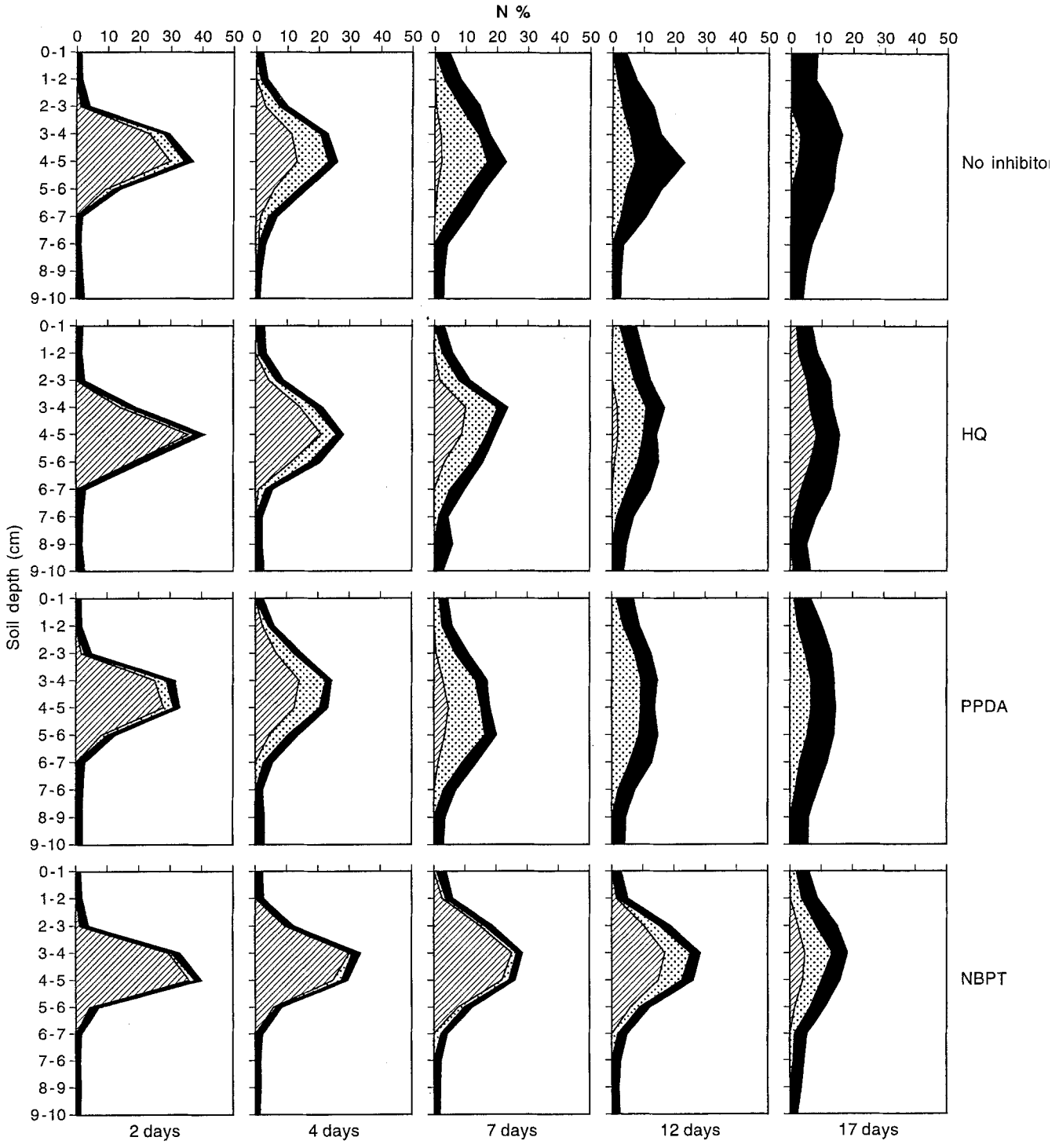

Fig. 3 Effect of urease inhibitors on N distriburion in soil profile at 10% moisture content, expressed as a percentage of the sum of urea N plus mineral N. The percentage indicated relates to a 1-cm layer of soil. For abbreviations, see Fig. 2. ▨ Urea N, ▩ NH_4^+-N, ■ (NO_2^++ NO_3^-)-N

Table 3 Recovery of urea N as a percentage of the urea N applied in the total soil column at 20% moisture content (for abbreviations see Table 2)

Inhibitor	Time (h)				
	2	4	7	12	17
None	49	16	0	0	0
HQ	43	31	2	0	0
PPDA	49	25	1	0	0
NBPT	61	56	38	23	2

Table 4 Mineral N in soil extracts after 17 days of incubation (for abbreviations see Table 2)

10% soil moisture		20% soil moisture	
Treatment	Mineral N (mg kg^{-1})	Treatment	Mineral N (mg kg^{-1})
No inhibitor	322.9	No inhibitor	302.9
HQ	336.6	HQ	291.1
PPDA	338.0	PPDA	282.5
NBPT	335.7	NBPT	304.9

the form of NH_4^+-N (Fig. 2a, c). Thereafter, it decreased due to the occurrence of nitrification. A clear increase in (NO_2^-+NO_3^-)-N, evenly distributed over the whole soil core, is shown in Figs. 2 and 3. However, in the hydroquinone treatment, the NH_4^+-N accumulation started later, and only 23% of the total urea N plus mineral N was in the NH_4^+ form after 4 days of incubation (Fig. 2b). Much less NH_4^+-N accumulated in the whole soil core with the NBPT-treated soil (Fig. 2d). The application of NBPT not only strongly retarted urea hydrolysis but also heavily influenced the distribution of different forms of N. The accumulated NH_4^+-N was only 12% after 7 days, reaching 33% after 17 days.

A significant difference in nitrification was observed between the uninhibited and inhibited soil cores. Nearly all of the NH_4^+-N was nitrified in the uninhibited sample (control) after 17 days while an important amount of NH_4^+ was still not nitrified in the inhibitor-treated samples, with even 12% of urea-N remaining in the treatment with NBPT. It was also clear that less (NO_2^-+NO_3^-)-N was produced upon application of the inhibitors (Fig. 3). However, the amount of (NO_2^-+NO_3^-)-N became roughly equal in all soil layers, in contrast to the other N compounds, which still showed the highest concentration in the layer of application. Moreover, without inhibitors only (NO_2^-+NO_3^-)-N reached the surface, while the application of inhi-

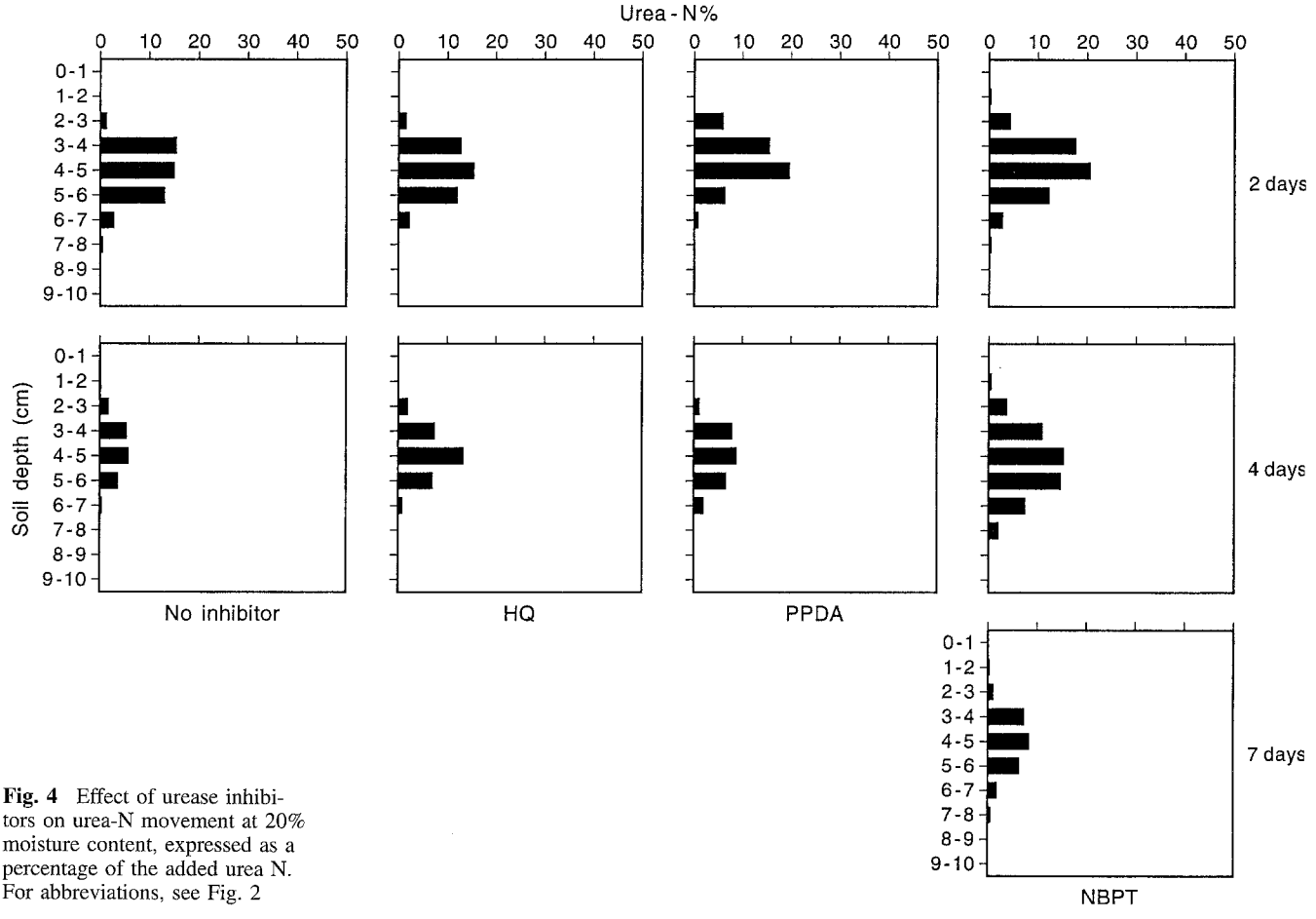

Fig. 4 Effect of urease inhibitors on urea-N movement at 20% moisture content, expressed as a percentage of the added urea N. For abbreviations, see Fig. 2

bitors ensured that some NH_4^+-N also reached the surface, so that more NH_3 volatilization became possible.

Influence of different urease inhibitors on urea-N movement at 20% moisture content

Increasing the soil moisture content resulted in a very strong increase in the urea hydrolysis rate, with a fast transformation of NH_4^+-N to NO_2^--N and NO_3^--N in consequence.

In the control treatment, only 49% of the applied urea was left after 2 days, which was more than 25% less than in the experiment at 10% moisture content (Table 3). After 4 days, only 16% of the added urea was left. After 7 days, the hydrolysis was completely finished. Hydroquinone and PPDA slightly slowed down the hydrolysis but the effect was not very clear until day 4. NBPT was still the most effective inhibitor among the three. However, even less urea remained than in the treatment at 10% moisture content. This indicates that the soil moisture content is a very important factor in urea hydrolysis. Apparently, the inhibitors were less effective at the higher moisture level. After 7 days of incubation, almost all of the applied urea was hydrolysed, except in the treatment with NBPT.

At the higher moisture content, the urea diffused faster. After 2 days of incubation, the remaining urea was distributed over a depth of 2–8 cm, which was deeper than in the treatment with 10% moisture (Fig. 4). In the NBPT treatment, a pronounced diffusion of urea was observed after day 4. A certain amount of NH_4^+-N (15–20% of the total) had accumulated after 2 days of incubation in most of the treatments except in the soil treated with NBPT, in which almost no NH_4^+-N accumulated for the whole period of incubation (Figs. 5, 6). It was also clear that the faster the hydrolysis, the more NH_4^+-N was found in the soil column. Meanwhile, more (NO_2^-+NO_3^-eously distributed over the soil column (Figs. 5, 6). The effective retardation of urea hydrolysis by NBPT resulted in a much lower NH_4^+-N accumulation throughout the soil column and the whole incubation period. Thus, all NH_4^+-N formed was quickly nitrified without any obvious accumulation (Fig. 6).

Table 4 shows that after 17 days of incubation, there were no significant differences in total mineral N in soil extracts from the samples treated with different kinds of inhibitor at 10% moisture content. A little more N than the applied urea-N (300 mg kg^{-1} of soil) was found. This was probably a reflection of the initial mineral N content (17 mg N kg^{-1}) and soil mineralization. However, upon increasing the soil moisture content from 10 to 20%, the mineral N in the soil extract clearly decreased (about

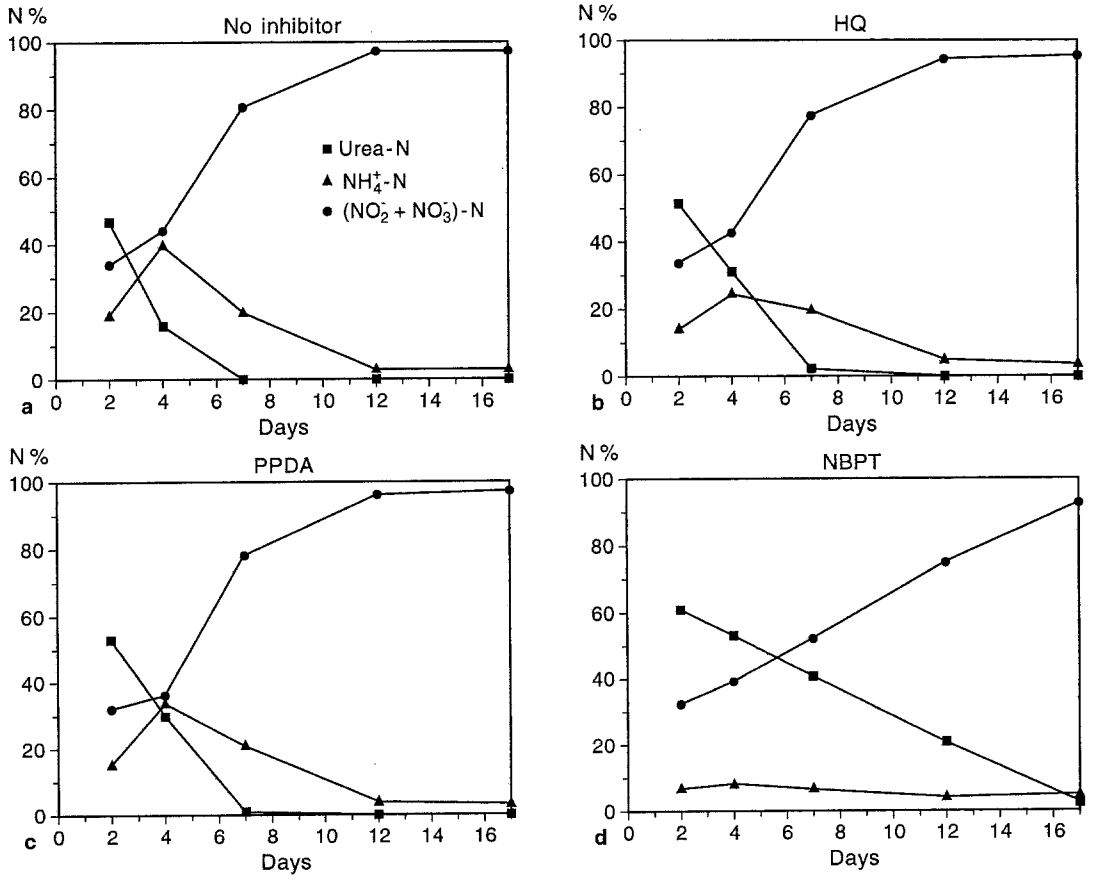

Fig. 5 Percentage distribution of different N compounds as influenced by urease inhibitors at 20% moisture content. For abbreviations, see Fig. 2

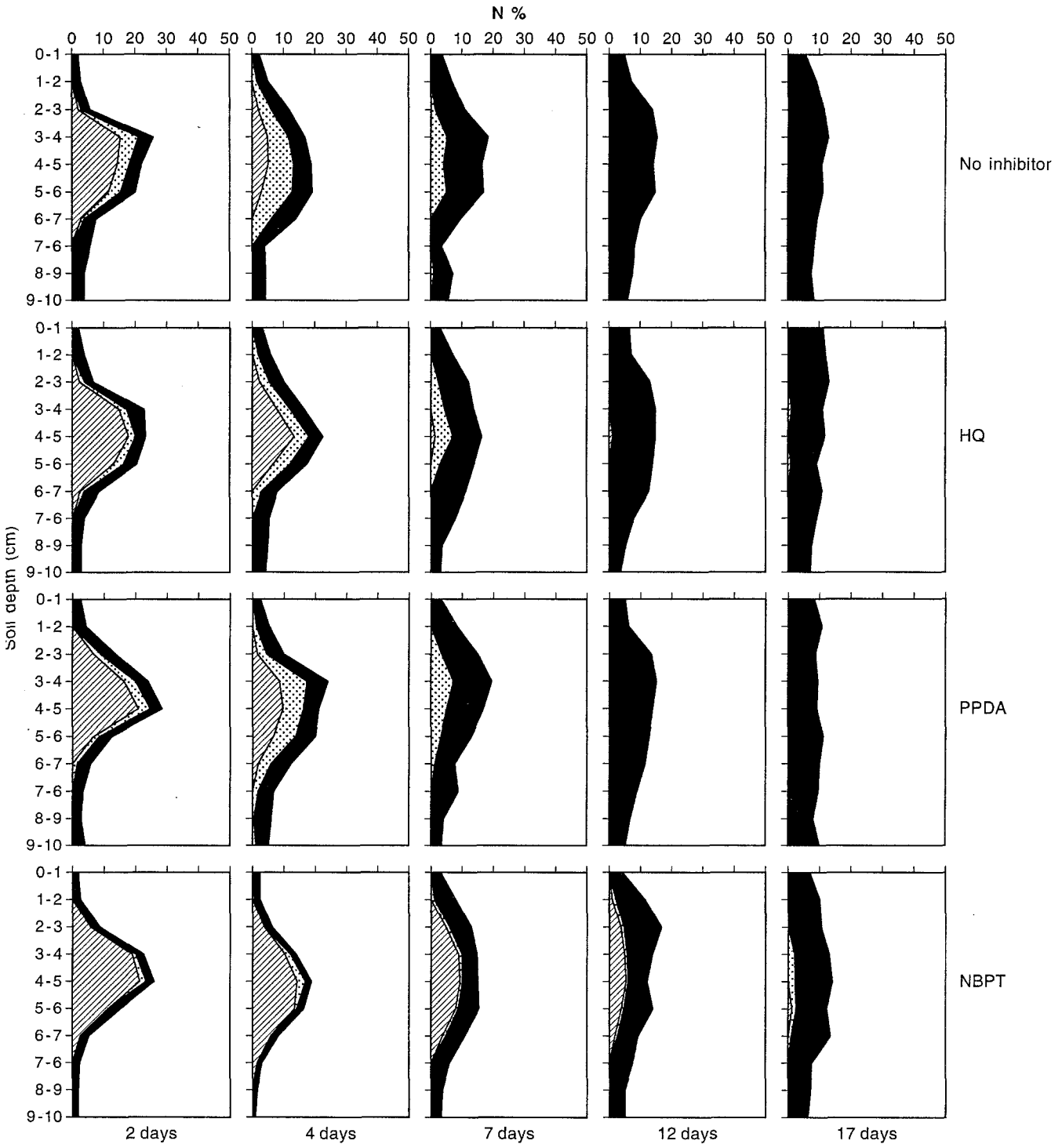

Fig. 6 Effect of urease inhibitors on N distribution in soil profile at 20% moisture content, expressed as a percentage of the sum of urea N plus mineral N. The percentage indicated relates to a 1-cm layer of soil. For abbreviations, see Fig. 2. ▨ Urea N, ⊠ NH_4^+-N, ■ (NO_2^-+ NO_3^-)-N

10%). This may have been due to denitrification in some microsites. Furthermore, since the soil columns had a diameter of 9.5 cm and a height of 10 cm, O_2 consumption in parts of the columns might have been higher than O_2 renewal, resulting in anaerobic pockets. Another possibility is that with a more rapid hydrolysis at a 20% moisture content, the pH became somewhat higher, resulting in more NH_3 loss. However, this possibility is less likely, since little NH_4^+ was observed in the end zones of the soil columns.

Discussion and conclusion

When urea was applied at a depth of 3–4 cm in a soil core instead of at the surface, the N loss through NH_3 volatilization may have been decreased. Clearly different patterns of N transformation were observed when different urease inhibitors were added. In the soil sample without any inhibitor, the applied urea was hydrolysed faster than in the other treatments, and the first hydrolysed product, NH_4^+ reached the highest concentration (55% of mineral N in the soil extract) after 7 days. Meanwhile, $NO_2^-+NO_3^-$ was formed by nitrification and accounted for 93% of the mineral N in the soil extract after 17 days of incubation. In the soil treated with hydroquinone urea hydrolysis was retarded. Therefore, a slower formation of NH_4^+ was observed and a longer time was necessary for completion of the nitrification process. Although PPDA did not show a clear retarding effect during the first 4 days, it still had some inhibitory effect on urea hydrolysis after 7 days and this delay resulted in a higher and longer accumulation of NH_4^+. NBPT was very effective in retarding urea hydrolysis, resulting in a very low formation of NH_4^+ and of $NO_2^-+NO_3^-$ during the first 7 days of incubation.

Urea movement and N transformation depended strongly on soil moisture. When the soil moisture content was raised from 10 to 20%, the time required to hydrolyse half the applied urea was decreased from 4 days to 2 days. This was mainly because the faster diffusion of urea-N created more contact between urea and the soil urease. A higher moisture content accelerated not only the urea hydrolysis but also soil nitrification.

$(NO_2^-+NO_3^-)$-N was fairly equally distributed over the soil column soon after the urea was applied. In contrast, for most of the time, urea and NH_4^+-N remained higher at the place where the urea had been applied.

Taking the displacement of urea, NH_4^+-N, and $(NO_2^-+NO_3^-)$-N into account, we observed that quite soon after the urea placement, in most cases, only $(NO_2^-+NO_3^-)$-N reached the surface of the column. Thus the risk of loss from NH_4^+ was reduced. Only a small N loss was observed at the end of the incubation in the treatments with 20% moisture content. This might have been due to denitrification in some microsites in the soil column. Some NH_3 volatilization cannot be excluded.

Hydroquinone and PPDA showed some inhibitory effects in retarding urea hydrolysis but NBPT was the most effective inhibitor. The influence of the inhibitors on urea hydrolysis clearly affected the distribution of different N forms.

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