NITRIFICATION INHIBITORS II. STUDIES WITH FURANO COMPOUNDS

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SUMMARY

The effects of furano compounds, furfural (furfuraldehyde) and furfuryl alcohol (5, 10, 20 and 30% of N applied) on nitrification of ammonium sulfate and urea N were studied in a sandy clay loam in laboratory. Both furfural and furfuryl alcohol significantly retarded the nitrification rates of both the fertilizers by inhibiting the conversion of NH_4^+ to NO_2^- without affecting the oxidation of NO_2^- to NO_3^- -N. 10, 20 and 30% concentrations of the compounds were effective up to 75 days with ammonium sulfate but more or less up to 45 days with urea.

INTRODUCTION

Nitrogenous fertilizers amended with nitrification inhibitors hold promise as a means of enhancing the efficiency of fertilizer nitrogen. These chemical agents when added to ammonium or ammonium forming fertilizers, not only minimize the losses of nitrogen by denitrification and leaching but also reduce nitrate contamination of ground and surface waters. Numerous compounds have been proposed for inhibiting nitrification in soils and several reviews have been published on the subject $1 \ 2 \ 3$.

In a previous paper⁵, it was reported that Karanjin the major furanoflavonoid from *Pongamia glabra* seeds is an effective nitrification inhibitor under laboratory and greenhouse conditions and compares well with the patented nitrification inhibitor, N-serve.

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Also the relationship between molecular structure and nitrification inhibition among karanjin and structural analogues suggest that furan ring in the molecule is responsible for this activity. This paper reports the effects of two simple and abundantly available furano compounds, furfural and furfuryl alcohol on nitrification in soils.

MATERIALS AND METHODS

The surface (0-15 cm) soil used was sandy clay loam from the Institute farm. The properties of the soil were described earlier⁵⁶. The soil was air dried and ground to pass a 2 mm screen before use.

Technical grades of furfural (boiling point, $160-162^{\circ}C$; density $1.16/20^{\circ}$) and furfuryl alcohol (boiling point, $170-171^{\circ}C$; density $1.13/20^{\circ}C$) were used. Preliminary work showed that analytical as well as technical grades of these compounds were equal in inhibiting nitrification but technical grades of furfural and furufuryl alcohol were chosen for economy. Karanjin was used to compare the effectiveness of furfural and furfuryl alcohol.

Samples of 200 g soil were transferred to 500 ml beakers and treated with 200 μ g N/g of soil from aqueous solution of ammonium sulfate or urea. Furfural and furfuryl alcohol were also applied to soils in their water solutions at rates of 0, 5, 10, 20, and 30 per cent of applied nitrogen. Karanjin was applied at 5 per cent level of nitrogen rate in acetone solution. The concentrations of furfural and furfuryl alcohol were chosen above 5 per cent because preliminary work indicated that these compounds show little, if any inhibition of nitrification when used at concentrations lower than 5 per cent⁴. The fertilizer and the inhibitors in solutions were first mixed together and then applied to soil and again thoroughly mixed with the soil. Enough water was added to bring the soil samples to 1/3 WHC moisture, the beakers were covered with polyethylene sheets and incubated at 30°C. Distilled water was added periodically to maintain the samples at 1/3 WHC moisture.

Duplicate 10 g soil samples were drawn and analyzed every 15 days for NH_4^+ , NO_2^- and NO_3^--N up to 75 days⁶. From the values of inorganic nitrogen obtained, the nitrification rates of ammonium sulfate and urea nitrogen without and with the addition of furfural furfuryl alcohol and karanjin were compared using the following formulae:

% nitrification rate =
$$\frac{(NO_2^- + NO_3^-) - N}{(NH_4^+ + NO_2^- + NO_3^-) - N} \times 100$$

RESULTS AND DISCUSSION

The results of the effects of furfural, furfuryl alcohol and karanjin on nitrification of ammonium sulfate and urea N in soil are summarized in Table 1. The nitrification rates of ammonium sulfate and

TABLE 1

Effects of furfural and furfuryl alcohol as compared to that of karanjin on the nitrification in soil treated with ammonium sulfate (AS) and urea N

Inhibitor	– Fertilizer	Nitrification rate (%) after days*				
		15	30	45	60	75
No inibitor	AS	17 abc	44 a	73 ab	86 a	94 a
	Urea	19 a	45 a	74 a	87 a	94 a
Karanjin, 5%	AS	6 de	17 d	39 g	62 e	86 cd
	Urea	6 de	$15 \mathrm{~de}$	40 g	60 e	83 de
Furfural, 5%	AS	14 bc	34 b	$68 ext{ cd}$	76 bc	90 abc
	Urea	8 d	26 с	69 bc	86 a	93 ab
Furfural, 10%	AS	7 de	28 c	67 cd	74 c	89 bc
	Urea	6 de	15 de	68 cd	84 a	93 ab
Furfural, 20%	AS	7 de	17 d	64 de	68 d	86 cd
	Urea	4 de	8 fg	47 f	84 a	92 ab
Furfural, 30%	AS	5 de	$8 \mathrm{fg}$	13 j	48 g	81 e
	Urea	3 e	5 g	25 h	76 bc	92 ab
Fur. alcohol, 5%	AS	13 c	35 b	71 abc	79 b	90 abo
	Urea	18 ab	42 a	74 a	86 a	94 a
Fur. alcohol, 10%	AS	7 de	15 de	61 e	68 d	89 bc
	Urea	13 c	27 с	67 cd	84 a	93 ab
Fur. alcohol, 20%	AS	5 de	9 fg	27 h	55 f	87 cd
	Urea	8 d	11 ef	47 f	79 Ъ	92 ab
Fur. alcohol, 30%	AS	3е	6 g	18 i	46 g	86 cd
	Urea	7 de	8 fg	25 h	76 bc	93 ab

* In each column means followed by a common letter are not significantly different at 5% level. The values are means of two replicates and LSD value for comparing any two days under the same treatment is 4%.

urea nitrogen in soils were similar and after 75 days, 94 per cent of nitrogen had nitrified in both the cases. With the addition of furfural or furfuryl alcohol or karanjin to the fertilizers significantly reduced their nitrification rates.

It was observed that the conversion of NH_4^+ to NO_2^--N was retarded by these compounds but the oxidation of NO_2^- to $NO_3^$ was not affected at any concentration. This resulted in conservation of NH_4^+-N and retardation of NO_3^--N formation in soil samples treated with these chemicals during 60 days depending on the concentration of the compounds.

The highest amount of NO₂--N realized from any treatment with and without the inhibitors was only 2.3 ppm, which supports that the conversion of NO₂- to NO₃--N was not affected by furfural and furfuryl alcohol. Evidently these compounds do not inhibit the Nitrobacter spp., responsible for conversion of NO_2^- to NO_3^--N in soils and this is desirable to prevent accumulation of toxic nitrite. The amounts of NO_2^--N in general remained low in all the treatments throughout and ranged from 0.0 to 2.3 ppm only.

Karanjin at 5 percent significantly retarded the nitrification rates of both urea and ammonium sulfate during 75 days (Table 1). These results are in accordance with our earlier report⁵. Furfural and furfuryl alcohol treatments also inhibited nitrification of both the fertilizers significantly and these effects appeared to match that of 5 per cent karanjin at 20 and 30 per cent concentrations of these chemicals during 45 to 60 days. The inhibition of nitrification by furfural and furfuryl alcohol suddenly decreased after 45 days while karanjin remained significantly effective even after 75 days. The results also indicate that though initially furfural appeared to be more effective with urea but both furfural and furfuryl alcohol significantly retarded the nitrification rates of ammonium sulfate nitrogen for a longer time than that of urea. This effect was more pronounced after 45 days, when only the nitrification of ammonium sulfate was inhibited by these chemicals. Furfuryl alcohol was mostly a significantly better inhibitor of ammonium sulfate N than that of urea.

CONCLUSIONS

The results of this study further support our earlier hypothesis that the furan ring in a molecule may impart nitrification inhibitory property to compounds⁵. This effect however can be further modified by varying the carbon chain length of the compound or secondly by the presence of an alkyl or aryl group (as in case of karanjin and analogues, see Sahrawat and Mukerjee⁵), in the structure. Preparation and screening of more furano compounds based on this thinking may yield more specific, cheap and effective nitrification-inhibitors. Furfural and furfuryl alcohol being cheap, abundantly available and effective in inhibiting nitrification of ammonium fertilizers (at 10% and higher rates) may find use for enhancing the fertilizer nitrogen efficiency. Work in our laboratory (K. L. Sahrawat *et al.*, unpublished work) further tend to indicate that the efficiency of furfural to inhibit nitrification of urea nitrogen can be significantly improved by preparing urea-furfural derivatives.

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