

## NITRIFICATION INHIBITORS FOR EFFICIENT USE OF FERTILIZER NITROGEN: A SCHEME FOR DEVELOPMENT OF NITRIFICATION INHIBITORS

K.L. Sahrawat

International Crops Research Institute for the  
Semi-Arid Tropics (ICRISAT), Hyderabad-500 016,  
INDIA

### ABSTRACT

Nitrification inhibitors are used for improving both quantity and quality of crops under situations where losses of fertilizer nitrogen due to leaching and denitrification are high. However, lack of cheap and specific inhibitors of nitrification curtails their practical use. A scheme has been proposed for developing specific efficient and cheap nitrification inhibitors based on two approaches -- (i) by evaluation of a large number of compounds possessing some sort of general biocidal activity for retarding nitrification in soils and (ii) by identification of the functional groups responsible for the activity and incorporating these groups in suitable compounds. Employing the second approach, it has been discovered that the furan ring in the compounds imparts the nitrification inhibitory property to varying degrees. This may be useful for practical agriculture.

### INTRODUCTION

It is now recognized that the use of chemicals for retarding nitrification in soils hold promise for improving both quantity and quality of crops under situations where nitrate formation causes the loss of fertilizer nitrogen due to leaching and denitrification (Gasser 1970, Prasad et al. 1971; Huber et al. 1977). These chemicals inhibit

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nitrification, helping to minimize subsequent losses due to leaching and denitrification (Prasad *et al.* 1971). However, it is known that these chemical agents do not completely check the nitrification process; instead they retard it by a sort of 'family planning' among mainly the *Nitrosomonas* group of nitrifying bacteria. It has also been realized that nonavailability of cheap specific and effective chemicals for regulating nitrification in soils is a bottleneck in exploiting their use for practical agriculture. There is an obvious need to develop nitrification inhibitors which are cheap and effective.

The characteristics desirable in a compound that is to function as a nitrification inhibitor include (i) it is imperative that it should be the specific blocker of the first step of nitrification, viz., conversion of  $\text{NH}_4^+$  to  $\text{NO}_2^-$  without affecting the subsequent oxidation of  $\text{NO}_2^-$  to  $\text{NO}_3^-$  and other useful biological processes in soils, (ii) it should be effective in retarding nitrification for reasonable periods at economical rates of application, and (iii) it must be inexpensive and abundantly available in the region of use.

The aim of this report is to describe a scheme that can be used to develop nitrification inhibitors which may be used effectively and economically for retarding nitrification in soils. The proposed scheme utilizes two approaches for the purpose.

#### SCHEME FOR DEVELOPMENT OF NITRIFICATION INHIBITORS

Firstly, by evaluation of a large number of compounds possessing a sort of general biocidal activity for retarding nitrification in soils, followed by testing of the effective ones in greenhouse and field trials.

Secondly, by identification of functional groups which impart nitrification-retarding properties to compounds. This could be done by studying the structure - nitrification - inhibitory activity relationships among compounds with proven ability to inhibit nitrification, along with study of their structural analogues. Later on

compounds could be selected with the said functional groups from those abundantly available and evaluated for their ability to retard nitrification. Alternatively, the functional groups imparting nitrification-inhibitory activity could be incorporated in inexpensive and abundantly available tailor made compounds with other desirable properties. Compounds found effective in the laboratory tests could be further tested in the greenhouse and or under field conditions to determine their value in improving fertilizer nitrogen efficiency.

During the last 15 years the first approach for selecting suitable compounds for retarding nitrification in soils has been employed, and numerous compounds have been tested for their value in retarding nitrification in soils and for their effects on crop production and fertilizer N efficiency (Gasser, 1970; Prasad *et al.* 1971; Hauck, 1972; Huber *et al.* 1977). The review of literature reveals that a vast array of compounds (including pesticides) [Sahrawat, 1974] possess nitrification-inhibitory activity to varying degrees. Since most of the studies involved a random screening of various compounds, hypothesis of structure - nitrification inhibitory activity relationships which could be helpful in identification of the functional groups responsible for such activity is rather difficult and the approach remains quite empirical. However, it is evident that compounds possessing some kind of biological activity can be exploited with advantage for their use as inhibitors of nitrification. As an example to support this approach, I cite the work of Bundy and Bremner (1973) who evaluated the effectiveness of 24 compounds proposed as inhibitors of nitrification in soils at 10 ppm concentration for 2 weeks. With the soil used, the effectiveness of the most potent inhibitors decreased in the order: 2-chloro-6-(trichloro-methyl) pyridine (N-serve) > 4-amino-1,2,4-triazole (ATC) > sodium or potassium azide > 2,4-diamino-6-trichloromethyl-s-triazine (CL 1580) > dicyandiamide > 3-chloroacetanilide > 1-amidino-2-thiourea > 2, 5-dichloroaniline > phenyl-mercuric acetate > 3-mercapto 1, 2, 4-triazole or 2-amino-4-chloro-6-methyl-

pyrimidine (AM) > sulfathiazole (ST) > sodium diethyldithiocarbamate. Several other compounds tested -- gallic acid, cysteine, cystine, methionine, methionine sulfoxide, methionine sulfone, ethionine, thiourea, 1-allyl-2-thiourea, and 2-mercapto-benzothiazole -- had little or no effect on nitrification of ammonium in soils. It was further suggested that the effectiveness of the inhibitors studied was markedly affected by soil type, soil temperature, and substitution of urea for ammonium sulfate as the source of nitrifiable nitrogen. The inhibitors were considerably more effective in light-textured soils and at 15°C than in heavy-textured soils and at 30°C.

#### IDENTIFICATION OF FUNCTIONAL GROUPS IMPARTING NITRIFICATION-INHIBITORY ACTIVITY

The second approach generated from our studies was carried out at the Indian Agricultural Research Institute, New Delhi, where we discovered that karanjin (3-methoxy furano-2,3',7,8-flavone), a furanoflavonoid from karanja (*Pongamia glabra*) -- a non-edible oil seed - is responsible for the nitrification-inhibitory activity observed with crude extractives from karanja cakes, as reported earlier (Sahrawat *et al.* 1974). Karanjin proved to be a potent inhibitor of nitrification in soil, matching the performance of Nitrapyrin (2-chloro-6-[trichloro-methyl] pyridine) of the Dow chemical company (Sahrawat and Mukerjee, 1977). The nitrification inhibitory activity of karanjin proved useful also in improving the yield and quality of rice in greenhouse pot culture studies (Sahrawat and Mukerjee, 1976, 1977). Results from these experiments are summarized in Table 1.

TABLE 1

Effects of karanjin on yield and composition of rice in greenhouse pot experiment (Sahrawat and Mukerjee, 1976, 1977)

| Crop particulars    | % increase by inhibiting nitrification |
|---------------------|--|
| Grain yield         | 31-54                                  |
| Grain + straw yield | 21-25                                  |
| Total N uptake      | 36-68                                  |
| Grain protein       | 2-14                                   |

Further studies where suitable alterations of the karanjin molecule: karanj ketone (4-hydroxy-5-*o*-methoxyacetyl coumarone), karanjondl (3-hydroxy furano-2', 3', 7, 8-flavone) and dihydrokaranjin (3-methoxydihydrofurano-2', 3', 7, 8-flavone) were prepared from karanjin and tested for their effects on nitrification showed that the furan ring present in the molecule seems to be the crucial structural factor for nitrification-inhibitory activity. All the compounds except for dihydrokaranjin where furan ring was absent, exhibited nitrification-retarding ability to varying degrees (Table 2).

TABLE 2

Effects of karanjin and its structural analogues on nitrification of urea N added to a sandy loam (Sahrawat and Mukerjee, 1977)\*

| Treatment              | Nitrification rate (%) after days |    |    |
|------------------------|-----------------------------------|----|----|
|                        | 15                                | 45 | 75 |
| Urea alone             | 14                                | 75 | 94 |
| Urea+karanjin          | 6                                 | 40 | 83 |
| Urea + karanj ketone   | 7                                 | 67 | 93 |
| Urea + karanjono1      | 10                                | 69 | 94 |
| Urea + dihydrokaranjin | 19                                | 74 | 94 |

\* Soil samples were treated with 200 ppm of N and with test compounds at the rate of 5% of N added and incubated under aerobic condition at 30°C. Nitrification rates were calculated from: % nitrification rate =

$$\frac{(\text{NO}_2^- + \text{NO}_3^-) - \text{N}}{(\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-) - \text{N}} \times 100$$

Preparation of urea furfuraldehyde derivatives may further help to enhance the effectiveness of furfural by checking its quick loss from soil (Sahrawat, K.L. *et al.* unpublished work).

The conclusion that furan ring imparts nitrification-inhibitory activity to compounds was further confirmed by our later studies, in which several furano compounds (based on furfuraldehyde including furfuraldehyde and furfuryl alcohol) showed varying degrees of ability to retard nitrification in soils (Sahrawat *et al.* 1977; Kuzvinzwa, 1974). Results with furfural and furfuryl alcohol are summarized in Table 3. Karanj and furfural are cheaply available and may find practical use in India.

TABLE 3

Effect of furfural and furfuryl alcohol on nitrification of urea N added to a sandy clay loam (Sahrawat et al. 1977)\*

| Treatment               | Nitrification rate % after days |    |    |
|-------------------------|---------------------------------|----|----|
|                         | 15                              | 30 | 45 |
| Urea alone              | 19                              | 45 | 74 |
| Urea + furfural         | 6                               | 15 | 68 |
| Urea + furfuryl alcohol | 13                              | 27 | 67 |

\* Soil samples were treated with 200 ppm of N and with test compounds at the rate of 10% of N added and incubated at 30°C under aerobic conditions. % nitrification rate =

$$\frac{(\text{NO}_2^- + \text{NO}_3^-) - \text{N}}{(\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-) - \text{N}} \times 100$$

It is evident that following either of the two approaches may lead to development of ideal types of compounds for use as nitrification inhibitors and improvement of the efficiency of fertilizer N under situations where nitrification causes losses due to denitrification and leaching. The first approach, being simple, could be used for short-term research goals in developing nitrification inhibitors from indigenous resources for a particular region or country. On the other hand, the second approach may be ideally suited for long range research activities on the subject and is undoubtedly a better and more scientifically sound procedure for developing suitable nitrification inhibitors. Information generated in laboratory tests of these chemical agents needs to be applied to determine the efficacy of the proposed compounds under pot culture and field conditions, so as to put their role as a crop-production tool in better perspective.

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## REFERENCES

- Bundy, L.G., Bremner, J.M. 1973: Inhibition of nitrification in soils. Soil Science Society of America Proceedings 37: 396-398.
- Gasser, J.K.R. 1970: Nitrification inhibitors: their occurrence, production and effects of their use on crop yields and composition. Soils and Fertilizers 33: 547-554.
- Hauck, R.D. 1972: Synthetic slow-release fertilizers and fertilizer amendments: In Goring, C.A.I., Hamaker, J.W. (eds) "Organic chemicals in the soil environment". Part B, p 633-690. Marcel Dekker, New York.
- Huber, D.M., Warren, H.L., Nelson, D.W., Tsai, C.Y. 1977: Nitrification inhibitors - new tools for food production. Bio Science 27: 523-529.
- Kuzvintzva, S.M. 1974: Furano - compounds as nitrification regulators. Unpublished M.Sc. thesis. Indian Agricultural Research Institute, New Delhi, p 65.
- Prasad, R., Rajale, G.B., Lakhdive, B.A. 1971: Nitrification retarders and slow - release nitrogen fertilizers. Advances in Agronomy 23: 337-383.
- Sahrawat, K.L. 1974: Effect of pesticides on nitrification. Pesticides (India) 8: 30-33.
- Sahrawat, K.L., Mukerjee, S.K. 1976: Effect of nitrification inhibitors on rice protein. Communications in Soil Science and Plant Analysis 7: 601-607.
- Sahrawat, K.L., Mukerjee, S.K. 1977: Nitrification inhibitors I. Studies with karanjin, a furanoflavonoid from karanja (Pongamia glabra) seeds. Plant and Soil 47: 27-36.
- Sahrawat, K.L., Mukerjee, S.K., Gulati, K.C. 1977: Nitrification inhibitors II. Studies with furano compounds. Plant and Soil 47: 687-691.
- Sahrawat, K.L., Parmar, B.S., Mukerjee, S.K. 1974: Note on the nitrification inhibitors in the seeds, bark and leaves of Pongamia glabra Vent. Indian Journal of Agricultural Sciences 44: 415-418.