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### PERSPECTIVES FOR RESEARCH ON DEVELOPMENT

OF NITRIFICATION INHIBITORS

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#### ABSTRACT

A brief review of the present status and scope of research on nitrification inhibitors pertaining to agricultural production and environmental pollution is presented. An approach is advanced for identification and evaluation of nitrification inhibitors from indigenous resources. Concurrently, research to identify functional groups retarding nitrification would be conducted. These approaches will aid in developing inexpensive and effective materials for nitrification inhibition. Future research needs relating to nitrification inhibitors are also examined.

#### INTRODUCTION

Fertilizers in general and N fertilizers in particular have made a major contribution toward agricultural productivity, but there is continuing need to improve the efficiency of N fertilizer use to

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achieve more efficient production of food and fiber and minimize fertilizer-related environmental stresses<sup>2,3,4</sup>. Low fertilizer N use efficiency is largely due to loss by denitrification, leaching or NH<sub>3</sub> volatilization<sup>2,3,5,6,7</sup>. These loss mechanisms (with the exception of NH<sub>3</sub> volatilization) are associated with and follow nitrification of native soil NH<sup>+</sup><sub>4</sub> or NH<sup>+</sup><sub>4</sub>-forming fertilizers to NO<sup>-</sup><sub>3</sub>-N.

Nitrogen use efficiency can be increased by agronomic and cultural practices (e.g. method of application and application of N during times of high plant demand)<sup>2</sup>. However, regulation of the nitrification rate in soils by use of nitrification inhibitors is becoming increasingly attractive. These chemicals retard nitrification in soils by slowing the rate of conversion of  $NH_4^+$ -N to  $NO_2^-$ -N but have no effect on the rate of oxidation of  $NO_2^-$ -N to  $NO_3^-$ -N. This will lessen the loss of N through leaching or denitrification in situations where these losses are high.

The large amount of literature on nitrification inhibitors<sup>8-15</sup> during the last two decades is testimony to the interest in this approach. However, to date only a few compounds have been adopted for agricultural use. The main problems are: (a) the high cost involved in the development and registration of effective nitrification inhibitors, (b) the economics of their use, and (c) the variable results often obtained<sup>10,14,16,17</sup>. Nevertheless, nitrapyrin (2-chloro-6-(trichloromethyl) pyridine) the nitrification inhibitor developed by Dow Chemical Co. USA<sup>18,19</sup> is approved for use in the USA. Dwell (5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole) (Olin Corp, USA) also was registered<sup>20</sup>, but apparently it is not being marketed. Dicyandiamide (DCD) is produced and marketed for use in West Germany<sup>17</sup> and is being evaluated in the USA.

The literature on nitrification inhibitors suggest that materials such as nitrapyrin are consistently effective in retarding nitrification (e.g., see Table 1 in Sahrawat and Keeney<sup>15</sup>). However their use has not necessarily increased crop yield or nitrogen use efficiency<sup>9,10,13,14,16,17,21,22</sup>. This research shows that the response of crops such as corn and wheat to nitrapyrin gives results that are affected by soil type, crop and the complex interactions between nitrogen cycle and nitrification inhibitors with the soil environment<sup>14,16,17,23</sup>. For example, the dissimilar mobility of the  $NH_4^+$  fertilizer and the nitrification inhibitor in soils can greatly affect its efficacy<sup>23</sup>.

Environmental variables such as soil pH and temperature increase nitrification rate and the rate of degradation of nitrification inhibitors<sup>14,23</sup>. Thus the prediction of effectiveness of nitrification inhibitors is difficult because of the complex interactions between soil and crop and the many environmental factors involved in the nitrogen cycle and nitrification inhibitors.

There is need to continue efforts to develop nitrification inhibitors that are inexpensive, readily available locally, and effective at reasonable rates of application. We deal here in some detail with the need for a structured approach (Fig. 1) to nitrification inhibitor research. Additionally, we propose some future research directions with examples emphasizing the use of indigenous materials available in different regions. This approach would involve coordinated research efforts from various disciplines including assessment of soil and environmental factors that affect bioactivity of nitrification inhibitors<sup>21</sup>.

#### DEVELOPMENT OF RESEARCH ON NITRIFICATION INHIBITORS

As shown in Fig. 1, there are two general approaches to developing effective nitrification inhibitors<sup>24</sup>. The first involves screening indigenous materials and compounds possessing some kind of biological activity. Efforts should be made to identify and inventory native products that have potential for retarding nitrification. A wide range of chemicals and materials that possess some type of biological activity should be screened for their nitrification inhibition activity. Rapid tests using soil and nitrifier cultures should first be used to screen these compounds and materials. Those found promising should then be evaluated in the greenhouse and field. The materials chosen for further tests must be inexpensive, readily available, and environmentally safe.

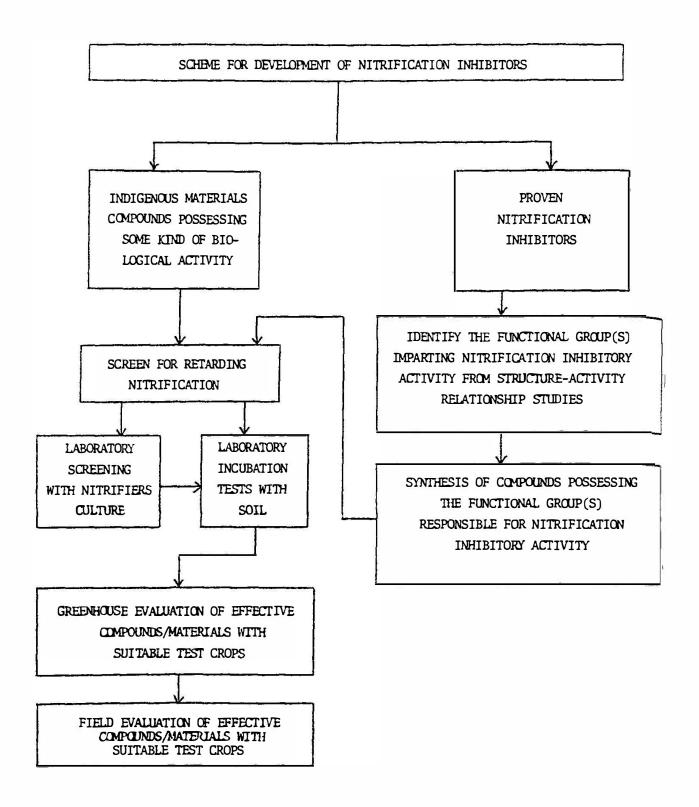


FIG. 1. SCHEME FOR DEVELOPING NITRIFICATION INHIBITORS.

For example, studies in India indicated that non-edible oil seed cakes and their derivatives have potential for retarding nitrification<sup>14,25</sup>. Among the seeds and cakes tested were Neem (<u>Azadiractha</u> indica L.) and Karanja (<u>Pongamia glabra</u> Vent.). These materials, especially neem cake, have been extensively tested<sup>14</sup>. Similarly, systematic studies with Karanja and its constituents have shown that the alcohol extracts of seeds and bark have potential for retarding nitrification in soil<sup>26</sup>. There are many other non-edible oil seed cakes and other natural plant products that might be screened<sup>25</sup>.

The second approach for developing nitrification inhibitors involves identification of the functional group or groups that impart nitrification inhibitory activity. This can be achieved by evaluating structure - nitrification inhibitory activity relationships. Briefly, this approach involves modifying the structure of known nitrification inhibitors by stepwise elimination or addition of the functional group(s) that may impart activity and by evaluating the original and the modified compounds for retarding nitrification in soil. Synthetic organic chemistry knowledge is a prerequisite for developing nitrification inhibitors based on this approach. However, it has the advantage that once the functional groups responsible for nitrification inhibitory activity are identified, inexpensive, effective nitrification inhibitors may then be synthesized from raw materials that are locally available.

A detailed study of structure activity relationships with Karanjin, a furanoflavonoid from the <u>Pongamia glabra</u> seeds, has established that the furan ring in the molecule is essential for the nitrification inhibitory activity of the compound<sup>27,28</sup>. A follow-up study with a number of compounds having the furan group attached to either alkyl or aryl ring has shown that this group imparts nitrification inhibitory to compounds to varying degree<sup>29,30</sup>.

# PERSPECTIVES

The use of nitrification inhibitors have potential in improving the efficiency of fertilizer N in the situations where the potential for loss of N due to denitrification or leaching is high. However, it should be emphasized here that the use of nitrification inhibitors  $m_{ay}$  not be profitable in improving crop yields and fertilizer efficiency especially for the plants which do not grow well with predominantly ammonium nitrogen<sup>14,31,32</sup>. This has been attributed to ammonium toxicity and/or to physiological effects when nitrogen nutrition is shifted to ammonium from nitrate<sup>15</sup>. It is also<sup>o</sup> possible that either the nitrification inhibitor or its degradation product could be phytotoxic<sup>15</sup>.

There are also reports that indicate that nitrification inhibitors may retard denitrification in some situations<sup>33</sup>. There is a clear need to delineate effects due to possible retardation of denitrification from those obtained by inhibition of nitrification.

Research is also needed to identify the action of nitrification inhibitors as to how they affect the form of nitrogen eventually made available to the plant. Use of  $^{15}N$  may be helpful for such research. The effect of inhibitors on the quality of different crops including the cation-anion balance due to shift to  $NH_4^+$  nutrition compared to  $NO_3^-$  nutrition imposed by the use of nitrification inhibitors  $^{15,34}$  must be evaluated.

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#### REFERENCES

- 1. Present address: International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), Patancheru P.O., A.P. 502324, India.
- Keeney, D. R. <u>In</u> Stevenson. F. J., R. D. Hauck, J. M. Bremner, D. R. Keeney (eds.) Nitrogen in Agricultural Soils, p. 605-649. Am. Soc. Agron., Madison, Wis., USA (1982).
- Delwiche, C. C. (ed.) Denitrification, Nitrification, and Nitrous Oxide. John Wiley, New York<sup>5</sup>, USA (1981).

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- 4. Greenwood, D. J. <u>In</u> Robertson, G. P., R. Herrera, T. Rosswall (eds.) Nitrogen Cycling in Ecosystems of Latin America and the Caribbean, Vol. 6, p. 45-60. Martin Nijhoff, The Hague (1982).
- 5. Savant, N. K., and S. K. DeDatta. Adv. Agron. 35, 241-302 (1982).
- Stevenson, F. J. (ed.) Nitrogen in Agricultural Soils. Am. Soc. Agron., Madison, Wis., USA (1982).
- 7. Vlek, P. L. G., I. R. P. Fillery, and J. R. Burford. Plant Soil 58, 133-175 (1981).
- Hauck, R. D. <u>In</u> Goring, C. A. I., J. W. Hamaker (eds.) Organic Chemicals in the Soil Environment, Part B, p. 633-690. Marcel Dekker, New York, USA (1972).
- Huber, D. M., H. L. Warren, D. W. Nelson, and C. Y. Tsai. BioScience 27, 523-529 (1977).
- 10. Meisinger, J. J., G. W. Randall, and M. L. Vitosh (eds.) Nitrification Inhibitors - Potentials and Limitations. Am. Soc. Agron., Madison, Wis. USA (1980).
- 11. Mulvaney, R. L., and J. M. Bremner. <u>In</u> Paul, E. A. and J. N. Ladd (eds.) Soil Biochemistry, Vol. 5, p. 153-196. Marcel Dekker, New York, USA (1981).
- 12. Parr, J. F. J. Environ. Qual. 2, 75-84 (1973).
- 13. Prasad, R., G. B. Rajale, and B. A. Lakhdive. Adv. Agron. <u>23</u>, 337-383 (1971).
- 14. Sahrawat, K. L. Plant Soil <u>57</u>, 335-352 (1980).
- 15. Sahrawat, K. L., and D. R. Keeney. J. Plant Nutr. <u>7</u>, 1251-1288 (1984).
- 16. Hagemann, R. W., and R. D. Meyer. California Agric. <u>34</u>, 14-15 (1980).
- Hauck, R. D., and H. Behnke (eds.) Proceedings of the Technical Workshop on Dicyandiamide. SKW Trostberg AG, West Germany (1981).
- 18. Goring, C. A. I. Soil Sci <u>93</u>, 211-218 (1962).
- 19. Goring, C. A. I. Soil Sci <u>93</u>, 431-439 (1962).
- 20. Emerson, S. Agrichem Age 26, 351, 37 (1982).
- 21. Varsa, E. C., S. L. Liu, and G. Kapusta. J. Fert. Issues <u>1</u>, 118-124 (1984).
- 22. Zublena, J. P. J. Fert. Issues 1, 7-14 (1984).

- 23. Keeney, D. R. <u>In</u> Meisinger, J. J., G. W. Randall, M. L. Vitosh (eds.) Nitrification Inhibitors - Potentials and Limitations, p. 33-46. Am. Soc. of Agron. Madison, Wis., USA (1980).
- 24. Sahrawat, K. L. In Ferguson, A. R., R. L. Bieleski, I. B. Ferguson (eds.) Plant Nutrition, p. 431-438. Proc. 8th Int. Colloq. on Plant Analysis and Fertilizer Problems. DSIR Information Series No. 134, Wellington, Govt. Printer, New Zealand (1978).
- 25. Vimal, O. P., and K. T. Naphade. J. Scient. Ind. Res. <u>39</u>, 197-211 (1980).
- 26. Sahrawat, K. L., B. S. Parmar, and S. K. Mukerjee. Indian J. Agric. Sci. 44, 415-418 (1974).
- 27. Sahrawat, K. L. Fert. News 26, 29-34 (1981).
- 28. Sahrawat, K. L., and S. K. Mukerjee. Plant Soil 47, 27-36 (1977).
- 29. Kuzvinzwa, S. M. M.Sc. Thesis, Indian Agricultural Research Institute, New Delhi (1974).
- 30. Sahrawat, K. L., S. K. Mukerjee, and K. C. Gulati. Plant Soil <u>47</u>, 687-691 (1977).
- 31. Haynes, R. J., and K. M. Goh. Biol. Rev. 53, 465-510 (1978).
- 32. Mills, H. A., and J. B. Jones, Jr. J. Plant Nutr. <u>1</u>, 101-122 (1979).
- 33. McElhannon, W. S., and H. A. Mills. J. Am. Hort. Sci. <u>105</u>, 673-67<sup>n</sup> (1981).
- 34. Sahrawat, K. L. <u>In</u> M. A. Scaife (ed.) Plant Nutrition, p. 570-575. Proc. 9th Int. Colloq. on Plant Nutrition, Warwick, Common W, Agric. Bureau, England (1982).