

EVALUATION OF CHELATING COMPOUNDS AND CARBOFURAN FOR INHIBITING NITRIFICATION IN SOILS

by K. L. SAHRAWAT*

Division of Agricultural Chemicals, Indian Agricultural Research
Institute, New Delhi 110 012, India

SUMMARY

Studies to evaluate 5 chelating compounds NTA (nitrilotriacetic acid), EDTA (ethylene diaminetetra acetic acid), tartaric acid, citric acid, thiourea and an insecticide, carbofuran as inhibitors of nitrification in a sandy loam (pH 7.7) at 10 and 50 ppm concentrations showed that except thiourea and carbofuran they had no appreciable effect on nitrification. Even thiourea and carbofuran were moderately effective at higher concentrations in retarding nitrification in soil at the most upto 3 weeks. The results of the study suggest that all the chelating compounds may not necessarily be inhibitors of nitrification process in soils as commonly believed and that carbofuran may have little effect on nitrification in soils with pH in the alkaline range under normal application rates.

INTRODUCTION

Lees⁵ postulated that compounds like guanidine, sodium diethylthiocarbamate, potassium ethyl xanthate and other organic compounds found to retard nitrification in soils (mainly oxidation of NH_4^+ by *Nitrosomonas*) are chelating agents. According to this theory, the metal enzyme involved in the oxidation of NH_4^+ to NO_2^- by *Nitrosomonas* is inhibited by these chelates, resulting in inhibition of nitrification. Based on this thinking it was decided to evaluate some chelating compounds like NTA (nitrilotriacetic acid), EDTA (ethylene diaminetetra acetic acid), citric acid, tartaric acid

* Present address: International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), 1-11-256, Begumpet, Hyderabad 500 016 A.P., INDIA

and thiourea for their possible effects on nitrification of ammonium sulfate and urea N in soil. It has been recognized that the use of nitrification inhibitors can be helpful both in conserving fertilizer N as well as in reducing the possibility of nitrate enrichment of ground and surface waters by NO_3^- derived from nitrification of fertilizer NH_4^+ . Numerous compounds have been proposed as inhibitors of nitrification in soils^{2 4 7}.

In another experiment, the effect of carbofuran on nitrification of $\text{NH}_4^+\text{-N}$ in soils was tested. This was done because carbofuran is an important insecticide having a wide usage for the control of insect pests of various crops through soil or foliar application. Though the persistence and degradation of this insecticide in soils have been studied by Getzin³. However, there is lack of information about the effect of carbofuran application on the transformation of ammonium nitrogen in soils. Also these agricultural chemicals are known to have effects on biochemical transformations like nitrification^{6 8 14} which may sometimes affect nitrogen nutrition of crops^{9 10}.

MATERIALS AND METHODS

The soil used was a surface (0–15 cm) sample of a sandy clay loam, alluvial soil collected from the farm of the Indian Agricultural Research Institute, New Delhi. Before use the soil was air dried and ground to pass a 2-mm sieve. The soil analysis was done as described by Sahrawat¹¹. The soil had pH, organic carbon, total N and C.E.C. of 7.7, 0.60%, 0.072% and 11.6 meq/100 g soil respectively.

Analytical reagents of thiourea, sodium salts of NTA (trisodium nitrilotriacetate monohydrate) and EDTA (disodium ethylenediaminetetraacetic acid), tartaric acid, citric acid and technically pure carbofuran (2,3-dihydro-2, 2-dimethyl-7-benzofuran-yl N-methyl carbonate) a product of FMC corporation, N.Y., were used for testing their effects on nitrification in soil at concentrations of 10 and 50 parts/ 10^6 of soil. The amounts of Na_3 NTA and Na_2 EDTA used were on the basis of free nitrilotriacetic acid and free ethylenediaminetetraacetic acid concentrations respectively. The ability of various chelating agents tested to inhibit nitrification in soil was compared with that of 2-chloro-6-(trichloromethyl) pyridine (N-Serve, a patented product of the Dow Chemical Co., Midland, Mich., USA) at a concentration of 10 $\mu\text{g/g}$ of soil.

The following procedure was used to study the effects of various compounds on nitrification of $(\text{NH}_4)_2\text{SO}_4$ and urea N. Samples (100 g) of soil were placed in 500 ml beakers and treated with 5 ml of water containing 10 mg of N as

urea or $(\text{NH}_4)_2\text{SO}_4$ and with 5 ml of water or 5 ml of water containing 1 mg or 5 mg of the compounds to be tested. More water was then added to the soil samples to bring them to 60% water-holding capacity (WHC) moisture level. The beakers were covered with polyethylene sheets and incubated at 30°C for 3 weeks. The moisture content of the soil samples was maintained by adding distilled water twice a week.

In a second incubation experiment, the effect of 10 and 50 ppm concentrations of carbofuran on nitrification of $\text{NH}_4^+\text{-N}$ in soil was studied for 4 weeks. Duplicate 10 g soil samples were drawn after thoroughly mixing the soil from each treatment and analysed weekly for NH_4^+ , NO_2^- and $\text{NO}_3^-\text{-N}$ ¹². From the values of NO_2^- and NO_3^- obtained from soil analysis the percentage inhibition of nitrification by the compounds tested was calculated as described by Bundy and Bremner¹, using the formula $(\text{C}-\text{S})/\text{C} \times 100$ where S = amount of $(\text{NO}_2^- + \text{NO}_3^-)\text{-N}$ produced in soil sample treated with the test compound and C = amount of $(\text{NO}_2^- + \text{NO}_3^-)\text{-N}$ produced in the control (no test compound added.)

RESULTS AND DISCUSSION

The results on the effects of different chelating compounds tested on nitrification of $(\text{NH}_4)_2\text{SO}_4$ and urea N in soil are given in Table 1. The results indicate that NTA, EDTA, tartaric acid and citric acid hardly had any appreciable effect on nitrification of fertilizer N. The percentage inhibition of nitrification with these compounds at 50

TABLE 1

Effects of chelating compounds and N-serve on nitrification of ammonium sulfate and urea nitrogen in soil

Compound	Amount of compound ($\mu\text{g/g}$ of soil)	% Inhibition of nitrification after weeks					
		Ammonium sulfate			Urea		
		1	2	3	1	2	3
NTA	10	2	0	0	2	0	0
NTA	50	6	0	0	4	0	0
EDTA	10	2	0	0	2	0	0
EDTA	50	7	1	0	5	0	0
Tartaric acid	10	3	0	0	2	0	0
Tartaric acid	50	6	2	0	4	1	0
Citric acid	10	2	0	0	0	0	0
Citric acid	50	4	0	0	3	0	0
Thiourea	10	10	7	2	7	3	0
Thiourea	50	18	14	7	16	7	3
N-serve	10	89	90	83	93	90	87

parts/ 10^6 concentration varied from 2 to 7% only after one week and the inhibition of nitrification was negligible after 2 weeks. There was little if any inhibition of nitrification observed with $10\mu\text{g/g}$ soil concentration of these compounds. However, thiourea showed some inhibition of nitrification of both urea and $(\text{NH}_4)_2\text{SO}_4$ N and the maximum inhibition observed at 50 parts/ 10^6 concentration was 18% after one week and ranged from 3 to 7% only after 3 weeks. At 10 parts/ 10^6 concentration, thiourea was considerably less effective in inhibiting nitrification and the maximum inhibition of nitrification observed was 10% after one week and ranged from 0 to 2% after 3 weeks. Table 1 also shows that as compared to 2-chloro-6-(trichloromethyl) pyridine (N-Serve), the compounds tested were little effective in inhibiting the nitrification of $(\text{NH}_4)_2\text{SO}_4$ or urea N in soil. The inhibition of nitrification of $(\text{NH}_4)_2\text{SO}_4$ N with thiourea has also been reported by Weir¹⁵.

The formation of NO_2^- -N from both urea and $(\text{NH}_4)_2\text{SO}_4$ was little influenced by any of the compounds tested. The maximum amount of NO_2^- detected was only about 5 parts/ 10^6 after one week and was less than 2 parts/ 10^6 after 3 weeks in all the treatments with urea. The amounts of NO_2^- -N accumulated with $(\text{NH}_4)_2\text{SO}_4$ was always less than 2 parts/ 10^6 after one week and NO_2^- was not detected after 3 weeks in all the treatments with or without the compounds tested.

It was further indicated from the results of the study that except thiourea to some extent, none of the compounds tested had any effect on conversion of either NH_4^+ to NO_2^- or oxidation of NO_2^- to NO_3^- so that the formation of both NO_2^- and NO_3^- from $(\text{NH}_4)_2\text{SO}_4$ or urea N in soil was little influenced. This finding seems to be somewhat incompatible with the theory forwarded by Lees⁵ that the chelating agents inhibit nitrification (mainly conversion of NH_4^+ to NO_2^-) in soils by chelating with some metal enzyme involved in the oxidation of NH_4^+ to NO_2^- by *Nitrosomonas*. NTA and EDTA are powerful chelating agents but these compounds could hardly make an impact in inhibiting the nitrification in soil treated with $(\text{NH}_4)_2\text{SO}_4$ or urea N even at a concentration of 50 parts/ 10^6 . The finding of Tabatabai and Bremner¹³ that NTA was readily decomposed by soil microorganisms under both aerobic and anaerobic conditions in Iowa soils at 30°C seems to support that NTA might be ineffective in inhibiting soil nitrification as found in the present study. The results of the present study suggest that all the chelating compounds

TABLE 2

Effect of carbofuran on nitrification in soil treated with ammonium sulfate (100 ppm N)

Carbofuran concentration ($\mu\text{g/g}$ of soil)	(NO ₃ ⁻ + NO ₂ ⁻)-N produced (ppm)				% Inhibition of nitrification			
	after weeks of incubation							
	1	2	3	4	1	2	3	4
0	19	40	58	70	—	—	—	—
10	17	37	56	68	10	7	3	3
50	14	30	50	67	26	25	14	4

may not necessarily be inhibitors of the nitrification process in soils as postulated by Lees⁵. Perhaps these compounds are inactivated either by soil metabolism or by physico-chemical phenomena; like adsorption with clay minerals or organic matter and are ineffective in inhibiting the nitrification process in soils unlike in studies with pure cultures of the nitrifying bacteria, where these factors are absent.

Results on the effect of Carbofuran on nitrification of ammonium sulfate nitrogen in soil are presented in Table 2. At 10 ppm the insecticide retarded nitrification only to a less extent. With the increase in the rate of application from 10 to 50 ppm, the inhibitory effect on nitrification was also increased but this lasted only upto 3 weeks. The maximum inhibition of nitrification observed by the insecticide was 26% after one week of application and this was reduced to 4% only after 4 weeks (Table 2).

It was also observed from the results that Carbofuran retarded both steps of the nitrification process *viz.* conversion of NH₄⁺ to NO₂⁻ and conversion of NO₂⁻ to NO₃⁻. The accumulation of NO₂⁻ in the soil samples increased with the increase in the rate of insecticide application. The maximum amounts of NO₂⁻ detected under different treatments mentioned in parentheses were 2.3 ppm (control) 7.0 ppm (10 ppm Carbofuran) and 10.5 ppm (50 ppm Carbofuran). However, the amount of NO₂⁻-N was less than 1 ppm after 5 weeks in all the treatments.

The inhibition of nitrification with Carbofuran application at both rates (10 and 50 ppm) seemed to last more or less upto 3 weeks in the soil studied. This might be probably due to rapid chemical hydrolysis of Carbofuran in this soil with an alkaline reaction of 7.7. The support for this has been provided by the study of Getzin³, who reported that the degradation of Carbofuran was 7–10 times faster in

an alkaline soil (pH 7.9) than in acid and neutral soils (pH 4.3–6.8).

The results of the present study along with the observations made by Getzin³ suggest that at field rates of application, Carbofuran will have little effect on the nitrification process in soils having pH in the alkaline range. Even the higher rate of application did not seem to appreciably retard nitrification in the soil used except for a temporary inhibition of nitrification upto 3 weeks. However, further studies with more soils providing a wide range in pH from acid through alkaline are necessary to substantiate this observation made in this preliminary study.

In conclusion the work reported suggests that the chelating compounds tested and carbofuran may be of little value for retarding nitrification in soils.

Received May 1977. Revised February 1978

REFERENCES

- 1 Bundy, L. G. and Bremner, J. M., Inhibition of nitrification in soils. *Proc. Soil Sci. Soc. Am.* **37**, 396–398 (1973).
- 2 Gasser, J. K. R., Nitrification Inhibitors: their occurrence, production and effects of their use on crop yields and composition. *Soils Fertil.* **33**, 547–554 (1970).
- 3 Getzin, L. W., Persistence and degradation of carbofuran in soil. *Environ. Entomol.* **2**, 461–467 (1973).
- 4 Hauck, R. D., Synthetic slow-release fertilizers and fertilizer amendments. *In* Organic Chemicals in the Soil Environment (C. A. I. Goring and J. W. Hamaker, Eds.) Part B, pp 633–690, Marcel Dekker, New York (1972).
- 5 Lees, H., The biochemistry of the nitrifying organisms – I; The ammonia oxidising systems of *Nitrosomonas*. *Biochem. J.* **52**, 134–139 (1952).
- 6 Parr, J. F., Effects of pesticides on microorganisms in soil and water. *In* Pesticides in soil and Water (W. D. Guenzi, Ed.) Soil Sci. Soc. Madison, Wisconsin (1974).
- 7 Prasad, R., Rajale, G. B. and Lakhdive, B. A., Nitrification retarders and slow-release nitrogen fertilizers. *Adv. Agron.* **23**, 337–383 (1971).
- 8 Sahrawat, K. L., Effect of pesticides on nitrification. *Pesticides India* **8**, 30–33 (1974).
- 9 Sahrawat, K. L., Effect of pesticides on nitrogen fixation. *Pesticides India* **9**, 21–23 (1975).
- 10 Sahrawat, K. L., Effect of pesticides on availability of plant nutrients. *Pesticides India* **10**, 15–18 (1976).
- 11 Sahrawat, K. L., Effect of biuret content on transformation of urea nitrogen in soil. *Soil Biol. Biochem.* **9**, 173–175 (1977).
- 12 Sahrawat, K. L. and Prasad, R., A rapid method for determination of nitrate, nitrite and ammoniacal nitrogen in soils. *Plant and Soil* **42**, 305–308 (1975).
- 13 Tabatabai, M. A. and Bremner, J. M., Decomposition of nitrilotriacetate (NTA) in soils. *Soil Biol. Biochem.* **7**, 103–106 (1975).
- 14 Tu, C. M. and Miles, J. R. W., Interaction between insecticides and soil microbes. *Res. Reviews* **64**, 17–65 (1976).
- 15 Weir, C. C., Effect of mixing thiourea with ammonium sulfate on nitrification of ammonia in a tropical soil. *Adv. Frontiers Plant Sci.* **13**, 195–198 (1966).