

EFFECTS OF PARATHION AND MALATHION ON TRANSFORMATIONS OF UREA AND AMMONIUM SULFATE NITROGEN IN SOILS

by K. L. SAHRAWAT*

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

KEY WORDS

Inhibition Nitrification Sandy loam Urea hydrolysis Urease

SUMMARY

A study of the effects of malathion and parathion applied at 10 and 50 $\mu\text{g/g}$ of soil on transformations of urea and $(\text{NH}_4)_2\text{SO}_4\text{-N}$ in a sandy loam showed that the insecticides retarded urea hydrolysis as well as nitrification of urea and $(\text{NH}_4)_2\text{SO}_4\text{-N}$. At 50 parts/ 10^6 rate of the insecticides, inhibition of urea hydrolysis ranged from 44 to 61% after 0.5 week and from 7 to 21% after 3 weeks of application. The insecticides inhibited the conversion of NH_4^+ to NO_2^- without appreciably affecting the subsequent oxidation of NO_2^- to NO_3^- -N. This resulted in accumulation of higher amounts of NH_4^+ -N in soil samples treated with ammonium sulfate or urea N.

The results suggest that transformations of urea and NH_4^+ fertilizers in soils may be influenced by the amount of organophosphorus insecticide present and this may affect plant nutrition and fertilizer use.

INTRODUCTION

Malathion and parathion are two of the organo-phosphorus insecticides currently having a wide usage. With the decline in the use of the chlorinated hydrocarbon insecticides, the use of these broad spectrum, relatively safer group of organo-phosphorus insecticides is expected to increase. However, it is well known that some of these organo-phosphorus insecticides (including malathion and parathion) are potent inhibitors of acetyl cholinesterase (See Melnikov⁹) and the side effects of these biologically active agricultural chemicals on sensitive microbiological processes like mineralization and nitrification of NH_4^+ fertilizers cannot be ruled out and sometimes these short time effects may be important for soil microflora and plant nutrition^{10, 11, 12}.

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

Though the fate and degradation of both malathion and parathion in soils have been well studied^{4, 5, 6, 8, 15, 16}, yet little information is available about their effects on the transformations of urea and NH_4^+ fertilizers. Recently Lethbridge and Burns⁷ have reported that accothion, thimet and malathion insecticides inhibited soil urease and checked urea hydrolysis by jackbean urease. This paper reports the effects of malathion and parathion insecticides on the transformations of ammonium sulfate and urea N in soil.

MATERIALS AND METHODS

The soil used was a surface 0–15 cm) sample of a sandy loam alluvial soil. The soil was air dried and ground to pass a 2 mm sieve before use and analysis reported in Table 1 was performed as described earlier¹³. Chemically pure, technical grades of both malathion (S-1,2-dicarbethoxyethyl)-0-0-dimethylthiophosphate) and parathion (0,0-diethyl 0-p-nitrophenylphosphorothioate) were used.

Table 1. Analysis of soil

pH	CEC (meq/ 100 g)	Organic C (%)	Total N (%)	Sand (%)	Clay (%)	WHC (%)	NH_4^+ -N ($\mu\text{g/g}$ soil)	NO_3^- -N ($\mu\text{g/g}$ soil)
7.7	8.9	0.58	0.07	70	17	32	1.5	8.6

Samples of 200 g soil were weighed in 500 ml beakers and treated with 100 μg N/g of soil from $(\text{NH}_4)_2\text{SO}_4$ or urea. The insecticides were dissolved in the minimum amount of acetone (1–2 ml) diluted with water and applied to soil at concentrations of 10 and 50 $\mu\text{g/g}$ soil. An equal amount of acetone was added to the soil samples without insecticide treatments. The beakers were kept open for about 2 hours to allow acetone to evaporate. Enough water was then added to the samples to bring them to 60% WHC moisture and the fertilizer and the insecticides were properly mixed with the soil. The samples were incubated at room temperature (mean 30°C, maximum 39°C and minimum 21°C) in beakers, covered with polyethylene sheets. The soil samples were maintained at 60% WHC moisture by periodically adding distilled water.

Ten g soil samples were analysed in duplicate for NH_4^+ , NO_2^- and NO_3^- -N weekly¹⁴. Soil samples incubated with urea were also analysed for urea-N in duplicate². The percentage inhibition of urea hydrolysis or nitrification of ammonium sulphate and urea N by malathion and parathion was calculated¹. Percentage inhibition of urea hydrolysis was calculated from $(A-B)/C-B \times 100$ where A = amount of urea found after incubation of soil treated with insecticides. B = amount of urea with control (no insecticide added) and C = amount of urea added. Percentage inhibition of nitrification of urea and $(\text{NH}_4)_2\text{SO}_4$ N was calculated from $(C-S)/C \times 100$ where S = amount of $(\text{NO}_2^- + \text{NO}_3^-)$ -N produced in the soil sample treated with insecticide and C = amount of $(\text{NO}_2^- + \text{NO}_3^-)$ -N found in the control (no insecticide added).

RESULTS AND DISCUSSION

Data on transformations of urea-N in soil (Table 2) showed that both insecticides retarded urea hydrolysis. There was more inhibition with parathion than with malathion at both rates of application. Urea hydrolysis was complete by 1 week without insecticide treatments. Urea hydrolysis was delayed up to 3 weeks by higher concentrations of malathion and parathion and was complete by 4 weeks. The inhibition of urea hydrolysis ranged from 30 to 61 per cent after 0.5 week and from 0 to 21 per cent after 3 weeks of application with both concentrations of the insecticides (Table 3). The rapid hydrolysis of untreated urea observed is not uncommon in soils with near neutral or above neutral pH^{1,13}.

Nitrification of $(\text{NH}_4)_2\text{SO}_4$ and urea N in soils was also inhibited by insecticide treatments. Parathion more severely inhibited nitrification of the ferti-

Table 2. Effects of malathion and parathion insecticides on the transformations of urea-N in soil*

Insecticide level ($\mu\text{g/g}$ soil)	Amounts of urea and inorganic N (parts/ 10^6) after weeks						
		0.5	1	2	3	4	5
0	Urea-N	8	0	0	0	0	0
	$\text{NH}_4\text{-N}$	58	43	30	18	8	5
	$\text{NO}_2\text{-N}$	5.0	5.4	2.9	3.4	1.0	0.0
	$\text{NO}_3\text{-N}$	21	40	59	73	84	91
Malathion 10	Urea-N	36	13	8	0	0	0
	$\text{NH}_4\text{-N}$	40	51	43	26	14	7
	$\text{NO}_2\text{-N}$	6.5	8.5	6.0	4.8	3.6	1.8
	$\text{NO}_3\text{-N}$	11	30	40	61	74	84
Malathion 50	Urea-N	49	29	20	11	0	0
	$\text{NH}_4\text{-N}$	37	65	60	51	39	15
	$\text{NO}_2\text{-N}$	3.0	5.0	8.8	10.0	6.8	3.0
	$\text{NO}_3\text{-N}$	2	3	5	21	46	71
Parathion 10	Urea-N	43	17	10	7	0	0
	$\text{NH}_4\text{-N}$	38	58	50	39	20	8
	$\text{NO}_2\text{-N}$	8.5	10.0	7.5	4.0	2.0	1.0
	$\text{NO}_3\text{-N}$	5	11	24	41	68	75
Parathion 50	Urea-N	64	35	30	21	0	0
	$\text{NH}_4\text{-N}$	22	60	54	50	42	19
	$\text{NO}_2\text{-N}$	4.0	5.8	10.5	8.0	7.2	4.6
	$\text{NO}_3\text{-N}$	2	2	2	14	34	63

* The amounts of $\text{NO}_2\text{-N}$ ranged from 0.0 to 1.5 parts/ 10^6 in all the treatments with and without insecticides after 6 weeks.

Table 3. Effects of malathion and parathion on urea hydrolysis in soil

Insecticide	Amount of insecticide ($\mu\text{g/g}$ soil)	% inhibition of urea hydrolysis after weeks				
		0,5	1	2	3	4
Malathion	10	30	13	8	0	0
Malathion	50	44	29	20	11	0
Parathion	10	38	17	10	7	0
Parathion	50	61	35	30	21	0

Table 4. Effects of malathion and parathion on nitrification of urea and ammonium sulfate nitrogen in soil

Insecticide	Amount of insecticide ($\mu\text{g/g}$ soil)	Inhibition of nitrification (%) after weeks										
		With ammonium sulfate						With urea				
		1	2	3	4	5	6	1	2	3	4	5
Malathion	10	29	29	12	10	6	3	15	26	14	9	6
Malathion	50	41	50	38	36	23	14	82	78	59	38	19
Parathion	10	36	40	33	34	18	18	54	49	41	18	16
Parathion	50	31	61	62	48	36	24	83	80	71	52	26

lizers (Table 4). The insecticides at 10 and 50 $\mu\text{g/g}$ soil rates considerably retarded the conversion of NH_4^+ to NO_2^- in soils treated with $(\text{NH}_4)_2\text{SO}_4$ or urea N. But the nitrification of urea N appeared to be more strongly inhibited during the first 3 weeks probably due to the lag created by inhibition of urea hydrolysis which delayed nitrification particularly at higher rates of the insecticides (Table 2). This resulted in accumulation of higher amounts of NH_4^+ -N treated samples over untreated $(\text{NH}_4)_2\text{SO}_4$ and urea.

Malathion and parathion did not appreciably affect the conversion of NO_2^- to NO_3^- -N but the amounts of NO_2^- -N tended to increase up to around 10 parts/ 10^6 with higher rates of malathion and both rates of parathion with urea N. But this amount of NO_2^- -N did not persist and after 5 weeks the amounts of NO_2^- -N in urea + insecticide treatments ranged from 0.0 to 1.5 parts/ 10^6 only. The highest amounts of NO_2^- -N accumulated with untreated $(\text{NH}_4)_2\text{SO}_4$ and urea N were only 1.8 and 5.4 parts/ 10^6 respectively. With $(\text{NH}_4)_2\text{SO}_4$ as the source of N the NO_2^- -N accumulation in samples treated with insecticides tended to increase but never exceeded 9.5 parts/ 10^6 and was very low after 6 weeks. With both the fertilizers, NO_2^- oxidation seemed to be little affected by the insecticide treatments and the maximum accumulation of NO_2^- (around 10 parts/ 10^6) occurred during first 2 weeks and then the amounts fell down quickly.

With the inhibition of conversion of NH_4^+ to NO_2^- by insecticide treatments, the rate of NO_3^- -N formation was greatly retarded in soil samples treated with both $(\text{NH}_4)_2\text{SO}_4$ and urea up to 5 weeks (Tables 2 and 4). The rate of nitrification of $(\text{NH}_4)_2\text{SO}_4$ appeared to be slower than that of urea. In case of untreated urea about 91% of the applied N had nitrified by 5 weeks but in case of $(\text{NH}_4)_2\text{SO}_4$ it took 6 weeks to attain this and this lag in nitrification of these fertilizers could be observed even after the first week. This difference in nitrification of urea and $(\text{NH}_4)_2\text{SO}_4$ could be due to high pH in the urea treated soil because oxidation of ammonium increases with the pH, although the oxidation of nitrite by *Nitrobacter* is markedly inhibited because of the toxicity of free ammonia to *Nitrobacter*³. It is interesting to note that nitrification rate of untreated $(\text{NH}_4)_2\text{SO}_4$ and urea treated with 10 parts/ 10^6 of malathion appeared to match more or less. This reduction in rates of hydrolysis as well as nitrification of urea can be an important factor in the efficient utilization of urea N.

With the higher rate of malathion and both rates of parathion, the amounts of NO_3^- -N realized were 20 to 30 per cent less than those obtained from untreated $(\text{NH}_4)_2\text{SO}_4$ even after 6 weeks when applied at 50 parts/ 10^6 though the effect was prominent even with 10 $\mu\text{g/g}$ soil rate of the insecticide.

To conclude, the work reported suggests that malathion and parathion insecticides may influence of NH_4^+ or NH_4^+ forming fertilizers by regulating their rates of mineralization in soils. This may be of significance to crops which can equally well utilize NH_4^+ -N. The rates of mineralization of fertilizers will be governed by the time of application and amounts of organophosphorus insecticides present in the soil. By proper timings of NH_4^+ fertilizers and organophosphorus insecticide applications to soil it may be possible to regulate N use by crops more efficiently in addition to pest management by the insecticides.

Received 13 March 1978. Revised April 1979

REFERENCES

- 1 Bundy, L. G. and Bremner, J. M. 1974 Effects of nitrification inhibitors on transformations of urea nitrogen in soils. *Soil Biol. Biochem.* **6**, 369-376.
- 2 Douglas, L. A. and Bremner, J. M. 1970 Extraction and colorimetric determination of urea in soils. *Soil Sci. Soc. Am. Proc.* **34**, 859-862.
- 3 Focht, D. D. and Verstraete, W. 1977 Biochemical ecology of nitrification and denitrification. *In Advances in Microbiol. Ecology*, vol. **1**, Ed. M. Alexander, Plenum Press, NY, 135-214.
- 4 Getzin, L. W. 1971 Partial purification and properties of soil enzyme that degrades the insecticide malathion. *Biochem. Biophys. Acta* **235**, 442-453.
- 5 Getzin, L. W. and Rosefield, I. 1968 Organo.phosphorus insecticide degradation by heat-labile substance in soil. *J. Agric. Food Chem.* **16**, 589-601.

- 6 Konrad, T. G., Chesters, G. and Armstrong, D. E. 1969 Soil degradation of malathion, a phosphorodithioate insecticide. *Soil Sci. Soc. Am. Proc.* **33**, 259–262.
- 7 Lethbridge, G. and Burns, R. G. 1976 Inhibition of soil urease by organo-phosphorus insecticides. *Soil Biol. Biochem.* **8**, 99–102.
- 8 Lichtenstein, E. P., Fuhremann, T. W. and Schultz, K. R. 1968 Effect of sterilizing agents on the persistence of parathion and diazinon in soils and water. *J. Agric. Food Chem.* **16**, 870–873.
- 9 Melnikov, N. N. 1971 *Chemistry of Pesticides*. Eds. F. A. Gunther and J. D. Gunther. Springer-Verlag, New York, pp. 303–386.
- 10 Parr, J. F. 1974 Effects of pesticides on microorganisms in soil and water. *In Pesticides in Soil and Water*. Ed. W. D. Guenzi. Soil Sci. Soc. Am. Madison, Wisconsin.
- 11 Sahrawat, K. L. 1974 Effect of pesticides on nitrification. *Pesticides India* **8**, 30–33.
- 12 Sahrawat, K. L. 1976 Effect of pesticides on availability of plant nutrients. *Pesticides India* **10**, 15–18.
- 13 Sahrawat, K. L. 1977 Effect of biuret content on transformations of urea nitrogen in soil. *Soil Biol. Biochem.* **9**, 173–175.
- 14 Sahrawat, K. L. and Prasad, R. 1975 A rapid method for determination of nitrate, nitrite and ammoniacal nitrogen in soils. *Plant and Soil* **42**, 305–308.
- 15 Walker, W. W. and Stojanovic, B. J. 1973 Microbial versus chemical degradation of malathion in soil. *J. Environ. Qual.* **2**, 229–232.
- 16 Wolfe, H. R., Staiff, D. C., Armstrong, J. F. and Comer, S. W. 1973 Persistence of parathion in soil. *Bull. Environ. Contam. Toxicol.* **10**, 1–9.