Bull. Environ. Contam. Toxicol. (1990) 44:948–954

Persistence of Carbamate Insecticides, Carbosulfan and Carbofuran in Soils as Influenced by Temperature and Microbial Activity

Anusmita Sahoo, Siddhartha K. Sahu, M. Sharmila, and N. Sethunathan

Laboratory of Soil Microbiology, Central Rice Research Institute, Cuttack 753006, India

Carbamate insecticides are used increasingly in agriculture as a replacement for environmentally more persistent organochlorines for broadspectrum control of insect pests of crops including certain insect pests not controlled by organochlorine or organophosphorus insecticides. Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl N-methylcarbamate), a broadspectrum insecticide, is one of the widely used carbamate insecticides in rice culture, especially for controlling brown planthopper (Nilaparvata lugens Stal), a major insect pest of great concern in areas of intensive cultivation of new high yielding rice varieties. Carbofuran is generally applied as granules to flooded rice paddies or as a spray to the basal portion of leaf sheath. Recently, an analog of carbofuran viz. carbosulfan (2,3-dihydro-2,2-dimethyl-7-benzofuranyl (di-ni-butyl)-aminosulfenyl) methylcarbamate) has been developed and recommended as a spray for use as an effective substitute for carbofuran. There is considerable literature on the fate and persistence of carbofuran in soil and water environments (Rajagopal et al. 1984). Carbofuran undergoes rapid chemical hydrolysis under alkaline conditions (at pH above 8.0) in buffer, water and soils (Fullmer 1977, Venkateswarlu et al. 1977, Seiber et al. 1978, Venkateswarlu and Sethunathan 1978, Siddaramappa and Seiber 1979, Chapman and Cole 1982). In contrast, available information indicates that its analog, carbosulfan is chemically stable under alkaline conditions, but undergoes rapid chemical hydrolysis (Ramanand 1989) to carbofuran and dibutylamine at pH below 6.0. Virtually, no information is available on the fate of this promising insecticide in soil and water. The present study is concerned with the persistence of carbosulfan and carbofuran in soils at 25 and 35°C.

MATERIALS AND METHODS

An alluvial soil (pH 6.2, organic matter 1.6%, total nitrogen (0.09%) from the experimental farm of Central Rice Research Institute, Cuttack, India and a laterite soil (pH 7.2, organic matter 0.6%, total nitrogen 0.04%) collected from Sukinda, India

Send reprint requests to N. Sethunathan at the above address.

were used. Technical grade carbosulfan (89.5% purity) and analytical grade carbofuran (99.4% purity) were gifts from FMC Corporation, Middleport, New York.

The soils were air-dried and ground to pass through a 2-mm sieve. Relative persistence of carbosulfan and carbofuran was studied in flooded alluvial soil. Portions (20 g) of sieved alluvial soil were placed in sterile glass test tubes (200 x 25 mm) and 25 mL of sterile distilled water were added to the soil to maintain flooded condition. Flooded alluvial soil was then incubated at 25 $\pm$ 1°C and 35 $\pm$ 1°C in B.O.D. incubator. After 10 days of incubation at respective temperatures, 0.1 mL of technical grade carbosulfan in ethanol and analytical grade carbofuran in 0.1 mL acetone containing 1 mg active ingredient of the insecticides were added to separate sets of test tubes and again incubated at corresponding temperatures. Duplicate samples were removed at periodic intervals for extraction and analysis of carbosulfan and carbofuran by gas-liquid chromatography (g.l.c.)

To determine the involvement of microorganisms in the hydrolysis of carbosulfan, 20-g portions of sieved alluvial and laterite soils were placed separately in sterile glass test tubes (200 x 25 mm) and adequate sterile distilled water was added to each tube to provide 60% water holding capacity. One set of test tubes of both soils was sterilized by autoclaving at 121°C for 1 h for three consecutive days. Sterile distilled water (25 mL) was subsequently added to non-autoclaved and autoclaved soil aseptically to provide flooded conditions. The flooded autoclaved and non-autoclaved soil were then incubated at 25 $\pm$ 1°C and 35 $\pm$ 1°C in B.O.D. incubator. After 10 days, 0.1 mL of carbosulfan (1 mg for alluvial soil and 1.5 mg for laterite soil) was added to each tube as described earlier. At periodic intervals, duplicate samples were analysed for carbosulfan and its hydrolysis product, carbofuran by g.l.c.

For residue extraction, the total contents (soil and water) in each tube were transferred to a 250-mL Erlenmeyer flask. Ethyl acetate (50 mL) and 20 g of anhydrous sodium sulfate were added to the flasks containing soil and water and shaken for 2 to 3 h. Residues in the ethyl acetate fraction were analysed in a Varian gas-chromatograph model 3400 equipped with a thermionic specific detector using a 5% OV-101 in a stainless-steel column. The operating conditions for carbosulfan were : argon (30 mL/min); hydrogen (3 mL/min); air (150 mL/min); column, 250°C; injector, 250°C; detector 270°C. For carbofuran, the same flow rates for gases were used; but column, injector and detector were maintained at 190, 240 and 250°C; respectively. The pH of soil samples were determined at regular intervals at 1:1.25 soil-water ratio.

RESULTS AND DISCUSSION

In a study on the persistence of carbosulfan and carbofuran in a flooded alluvial soil, both insecticides disappeared more rapidly

Table 1. Persistence of carbosulfan and carbofuran in flooded alluvial soil held at 25 and 35°C

Incubation (days)	Residues recovered in ug. 20 g^{-1} soil					
	Carbosulfan				Carbofuran	
	25°C		35°C		25°C	35°C
0	680±50	(0)[a]	785±45	(0)	880±45	976±45
2	450±10	(0)	375±45	(85± 5)	530±30	385±15
4	285±15	(230±0)	80± 0	(360± 0)	510±50	235±35
6	244± 6	(317±33)	0	(422±22)	420±40	208± 8
10	160±20	(355±10)	0	(235± 0)	370± 5	100± 5
30	20±10	(550±10)	0	(125± 5)	260± 5	35±10

[a] Figures in parentheses denote the amount of carbofuran formed from carbosulfan.

The detection limit was 1 ng for carbofuran and 2 ng for carbosulfan.

Table 2. Persistence of carbosulfan in sterilized and nonsterilized flooded alluvial soil held at 25 and 35°C

Incubation (days)	Residues recovered in ug.20 g^{-1} soil			
	25°C		35°C	
	Sterilized	Nonsterilized	Sterilized	Nonsterilized
0	890±40 (0)[a]	800±40 (0)	950±30 (0)	890±30 (0)
4	780±20 (0)	480±45 (148±12)	920±20 (0)	40±10 (305± 5)
6	775±25 (0)	362±12 (172±18)	875±10 (0)	0 (422±38)
10	700± 5 (0)	315±10 (180± 5)	880±10 (0)	0 (305±10)
30	700±20 (0)	0 (210±10)	740±20 (0)	0 (0)

[a] Figures in parentheses denote the amount of carbofuran formed from carbosulfan.

Table 3. Persistence of carbosulfan in sterilized and nonsterilized flooded laterite soil held at 25 and 35°C

Incubation (days)	Residues recovered in ug. 20 g^{-1} soil			
	25°C		35°C	
	Sterilized	Nonsterilized	Sterilized	Nonsterilized
0	1060±15 (0)[a]	1030±15 (0)	1270± 0 (0)	1270± 0 (0)
4	1060±30 (0)	650±60 (0)	1230±40 (0)	340±60 (130±10)
8	1060± 0 (0)	250±10 (200±0)	1080±15 (0)	180±10 (220± 0)
12	1120±30 (0)	165±35 (437±7)	970±10 (0)	100±25 (422± 8)

[a] Figures in parentheses denote the amount of carbofuran formed from carbosulfan.

at 35°C than at 25°C (Table 1). Carbosulfan was degraded distinctly faster than carbofuran at both temperatures. Thus, the concentration of carbosulfan declined to undetectable levels in 6 days at 35°C and to negligible levels after 30 days at 25°C; but, the amount of carbofuran recovered from carbofuran-amended soil was more than 20% of the original level after 6 days at 35°C and 25% even after 30 days at 25°C. The degradation of carbosulfan in soil at both temperatures proceeded by hydrolysis, at a faster rate of 35°C than at 25°C, with concomitant accumulation of carbofuran as its hydrolysis product in substantial amounts. Carbofuran, formed from carbosulfan, also disappeared faster at 35°C than at 25°C as noticed with carbofuran applied to the soil. Carbosulfan is known to undergo fairly rapid chemical hydrolysis in buffer or water at pH below 6.0 (Ramanand 1989). Exceptionally rapid hydrolysis of carbosulfan in flooded soil, at 35°C in particular, raises the question whether this hydrolysis is mediated chemically, biologically or both. When carbosulfan was added to the 10-day preflooded soil, the pH of the soil was 6.9 to 7.1. No appreciable change in pH occurred during further incubation of the soil for 30 days after insecticide addition. At this pH range, carbosulfan is relatively stable (Ramanand 1989). The rapid hydrolysis of carbosulfan in the soil is probably not related to pH.

In a follow-up experiment, microbial role in the hydrolysis of carbosulfan was examined by comparing its loss from sterilized (autoclaved) and nonsterilized alluvial soil under flooded conditions. As in the earlier experiment, hydrolysis of carbosulfan proceeded more rapidly at 35°C than at 25°C in non-sterilized soil with concomitant accumulation of carbofuran in substantial amounts (Table 2). In sterilized soil, no appreciable degradation of carbosulfan occurred during 30-day incubation and no carbofuran was formed from carbosulfan. The pH of both sterilized and nonsterilized soil at the time of insecticide addition (10 days after flooding) and during 30-day incubation after insecticide addition was 6.9 to 7.1.

The persistence of carbosulfan was studied in sterilized and non-sterilized samples of laterite soil under flooded conditions. Degradation of carbosulfan occurred only in nonsterilized soil (Table 3). As in alluvial soil, a rise in temperature from 25 to 35°C increased the hydrolysis of carbosulfan to carbofuran in nonsterilized soil samples. Carbosulfan appeared to be more persistent in laterite soil (Table 3) than in alluvial soil (Table 1); because, substantial amount of carbosulfan was recovered from nonsterilized soil after 12 days even at 35°C. The pH of laterite soil was 6.9 to 7.1 during 30-day incubation.

Persistence of carbosulfan in sterilized soils suggests that this insecticide is chemically stable in soils of near neutral pH. Substantial hydrolysis of carbosulfan in nonsterilized soils, and not in sterilized soils, indicates that microorganisms are involved in its hydrolysis.

Acknowledgements. We thank our Director, Dr. S. Patnaik for permission to publish this work and University Grants Commission, New Delhi for awarding a research fellowship to Mr. S.K. Sahu. This project was supported by US-India Funds (Grant No.FG-In-693).

REFERENCES

Chapman RA, Cole CM (1982) Observations on the influence of water and soil pH on the persistence of insecticides. J Environ Sci Health 17 B : 487-504

Fullmer OH (1977) FMC Corporation, Agricultural Chemical Division Richmond, California

Rajagopal BS, Brahmaprakash GP, Reddy BR, Singh UD, Sethunathan N (1984) Effect and persistence of selected carbamate pesticides in soils. Residue Rev 93 : 1-207

Ramanand K (1989) Studies on factors affecting persistence of insecticides in rice soils. Ph.D. thesis, Utkal University, Bhubaneswar, India. pp. 181

Seiber JN, Catahan MP, Barrill CR (1978) Loss of carbofuran from rice paddy water : Chemical and physical factors. J Environ Sci Health 13B : 131-148

Siddaramappa R, Seiber JN (1979) Persistence of carbofuran in flooded rice soils and water. Prog Water Technol 11 : 103-111

Venkateswarlu K, Gowda TKS, Sethunathan N (1977) Persistence and biodegradation of carbofuran in flooded soils. J Agric Food Chem 25 : 533-536

Venkateswarlu K, Sethunathan N (1978) Degradation of carbofuran in rice soils as influenced by repeated application and exposure to aerobic conditions following anaerobiosis. J Agric Food Chem 26 : 1148-1151

Received September 9, 1989; accepted November 21, 1989