Bull. Environ. Contam. Toxicol. (1991) 46:374–379

Bulletin of Environmental Contamination and Toxicology

Fate of ^{14}C-Carbaryl in Soils as a Function of pH

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Carbaryl (1-naphthyl, N-methyl carbamate), introduced as a replacement for persistent organochlorine compounds, is generally used as a broad-spectrum insecticide against over 150 pests at rates ranging from 0.57 to 4.5 Kg a.i./ha. Carbaryl hydrolyzes to 1-naphthol, methylamine and carbon dioxide in aqueous solutions (Vontor et al. 1972). The stability of carbaryl increases with decreasing pH (Aly and El-Dib 1971; Larkin and Day 1985). The importance of pH on the fate of carbaryl, its stability, bioavailability and toxicity in aquatic environment has already been reported (Fisher and Lohner 1986). Rajagopal et al. (1984) have reviewed the fate and persistence of carbaryl in soils. However, information on the fate of carbaryl in soil environment as a function of pH with respect to the formation of extractable and non-extractable (soil bound) residues is limited. Here we report studies on the fate of carbaryl in three soils with varying pH values.

MATERIALS AND METHODS

Carbaryl having an assay of 100% was obtained from Union Carbide Corp., New York, USA. Ring labelled ^{14}C-carbaryl (carbaryl-naphthyl-1-^{14}C with a specific activity of 3.11 mCi/g (98.9% radiochemical purity) was obtained from International Atomic Energy Agency,Vienna,Austria. Analytical grade 1-naphthol was procured from Sigma Chemical Co.,St.Louis,USA. The characteristics of soils used are shown in Table 1.

Carbaryl (150 μg of unlabelled and 50 μg of labelled) dissolved in benzene was added to 20 g soil (air-dry basis) in glass test tubes (200 x 20 mm dia.) to obtain a concentration of 10 ppm in the soil. After solvent evaporation the treated soil was thoroughly mixed to ensure uniform distribution of the chemical. The moist

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Table 1. Soil characteristics

Soil	pH	O.C. %	Sand	Silt	Clay
				%	
Sandy clay	4.2	1.18	50.8	13.0	36.2
Sandy loam	6.8	0.43	46.0	22.0	22.0
Clay	8.3	0.66	9.0	21.0	70.0

condition (60% Water Holding Capacity) was maintained by adding distilled water to one set of tubes with soils. For flooded condition, another set of tubes with soils were flooded with water to a level of 5 cm above soil surface. The tubes were plugged with cotton and incubated at 28-30°C for periods ranging from 7 to 56 days. Loss of water by evaporation was periodically compensated by addition of distilled water. At each sampling period, two tubes for each treatment were analyzed.

Carbaryl from soils was extracted with a mixture of acetone and water (1:1) and partitioned with chloroform (Rodriguez and Dorough 1977). The chloroform extracts were chromatographed on Silica gel-C F254 (Acme Synthetic Chemicals, Bombay) thin-layer plates (0.25 mm thickness) using ether : hexane (4:1) solvent system (Locke 1972). Authentic standards were also similarly chromatographed for comparison. The areas on thin-layer plates corresponding to authentic standards were scrapped into scintillation vials and radioactivity was determined using a Packard Tricarb Model 3255 scintillation spectrometer. The scintillation fluid was of the following composition: PPO, 5g: naphthalene, 100g; dioxane, 1000ml. The extracted soils were combusted in a Biological Material Oxidizer (Harvey Inst.,N.J., USA) using Oxysolve-C scintillation fluid to assay the soil bound residues. Soil organic matter was fractionated using a standard procedure (USEPA 1975). The radioactivity in samples was corrected for quenching and background activity.

RESULTS AND DISCUSSION

The extractable ^{14}C-residues were more in sandy clay and sandy loam than in clay soil both under moist and flooded conditions (Table 2). In sandy loam and clay soils the extractable ^{14}C-residues decreased with time; however in sandy clay soil there was initial decrease upto 14-day incubation period and remained more or less at the same level upto the end of experiment. In

Table 2. Distribution of ^{14}C-radioactivity in ^{14}C-carbaryl treated soils

		Soil treatment			
		Moist		Flooded	
		% of applied ^{14}C recovered as			
Soil	Incubation (Days)	Extractable	Soil bound	Extractable	Soil bound
Sandy clay (pH 4.2)	7	72.6	-	77.2	-
	14	39.7	-	31.6	-
	56	36.4	12.5	37.4	15.3
Sandy loam (pH 6.8)	7	63.9	-	70.7	-
	14	17.6	-	27.4	-
	56	7.6	35.7	16.1	41.0
Clay (pH 8.3)	7	24.7	-	26.1	-
	14	8.0	-	5.9	-
	56	4.5	78.0	3.8	92.0

general flooding the soil had no influence on the extractable ^{14}C-residues.

The solvent extracts of three soils were further partitioned with chloroform. All the radioactivity could be recovered in the chloroform fraction which indicated that the polar metabolites of carbaryl were absent in soils. Thin-layer chromatography of chloroform extracts revealed the presence of the

Table 3. Distribution of carbaryl and 1-naphthol in ^{14}C-carbaryl treated soils

		Soil treatment			
		Moist		Flooded	
		% of applied ^{14}C as			
Soil	Incubation (Days)	Carbaryl	1-naphthol	Carbaryl	1-naphthol
Sandy clay (pH 4.2)	7	57.3	0.20	63.6	1.05
	14	37.8	0.60	26.3	0.04
	56	32.1	0.20	32.3	0.04
Sandy loam (pH 6.8)	7	56.6	0.27	42.6	0.11
	14	14.6	0.20	19.4	0.30
	56	6.4	0.10	12.5	0.30
Clay (pH 8.3)	7	16.0	0.31	19.1	0.86
	14	1.8	0.10	1.6	0.10
	56	1.0	0.04	0.4	0.05

parent compound and its metabolite, 1-naphthol (Table 3). Carbaryl was more persistent in sandy clay soil than in clay soil under both moist and flooded conditions. The pattern of persistence of carbaryl in three soils over a period of time is influenced by pH of the soil. Thus at the end of 56 days, the percent carbaryl recovered was 32.1,6.4 and 1.0 in sandy clay,sandy loam and clay soils respectively. A similar trend was seen in flooded soils. 1-naphthol was formed in very low amounts.

Kazano et al.(1972) found that most of the radioactivity in solvent extracts of carbonyl ^{14}C-carbaryl treated soils was the result of intact carbaryl and only 0.25% of the radioactivity was distributed among the degradation products. Rodriguez and Dorough (1977) reported that solvent extracts of ring ^{14}C-carbaryl treated soils consisted mainly of the parent compound. However, 1-naphthol was reported to be the major degradation product of carbaryl in soils(Rajagopal et al. 1983; Rajagopal and Sethunathan 1984).

Soil bound residues were examined only at the end of final incubation period of 56 days and the results are presented in Table 2. The bound residues were high in clay soil as compared to sandy clay soil under both moist and flooded conditions. There appears to be a correlation between soil pH and bound residues formation; increase in soil pH being reflected in increased bound residues. Between moist and flooded conditions, bound residues were marginally higher in the latter. Although formation of soil bound residues with carbaryl has been reported (Kazano et al. 1972; Rodriguez and Dorough 1977; Rajagopal and Sethunathan 1984; Murthy and Raghu 1988), they were not examined in

Table 4. Distribution of ^{14}C-radioactivity in soil organic matter of ^{14}C-carbaryl treated soils

Soil	Treatment	% ^{14}C present in Fulvic acid	Humic acid	Humin
Sandy clay	Moist	10.1	3.3	86.4
(pH 4.2)	Flooded	9.6	3.8	86.5
Sandy loam	Moist	19.2	1.9	78.9
(pH 6.8)	Flooded	16.0	1.8	82.1
Clay	Moist	10.7	1.9	87.2
(pH 8.3)	Flooded	9.6	1.6	88.8

relation to soil pH. The soil organic matter was fractionated to see the distribution of soil bound residues (Table 4). The humin portion of soil organic matter accounted for most of the ^{14}C-bound residues. Between fulvic and humic acids, the former contained more of the ^{14}C-bound residues. The association of the the ^{14}C-residues with fulvic acid implies that it may render them mobile in the soil environments (Khan 1980).

Comparison of ^{14}C-mass balance in the three soils showed good recovery in clay soil than other two soils. Kazano et al. (1972) also obtained good recovery of carbaryl as extractable and non-extractable residues. Further they observed mineralization in sandy soils. Although, the objective of the present experiment is not aimed at determining the total budgetting of the added ^{14}C-carbaryl, the low recoveries in sandy clay and sandy loam soils may stem from possible mineralization of carbaryl. In conclusion it may be stated that increase in soil pH decreased extractable carbaryl residues and increased soil bound residues.

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Received December 1, 1989; accepted October 1, 1990.