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Persistence of Phorate and Carbofuran in Relation to Their Effect on the Mineralization of C, N, and P in Alluvial Soil

A. C. Das, D. Mukherjee

Department of Agricultural Chemistry and Soil Science, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur—741252, India

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Soil is the repository of all types of chemical inputs including insecticides, generally applied to the crop fields to combat insect pests for better crop production. As organic substance of any kind cannot escape the onslaught of microbial degradation, insecticides are no exceptions. Generally, insecticidal residues are degraded by soil microorganisms to derive energy, carbon and other nutrients for their growth and metabolism (Bollag 1982) resulting in an increase in population of active microoganisms which favourably influence the transformation of plant nutrients in soil (Rangaswamy and Venkateswarlu 1993). On the other hand, there are some insecticides which have deleterious effect on the activities of benefical microorganisms in soil. Yet, those insecticides are degraded in soil through cometabolism. The insecticidal effects on soil microorganisms and their associated transformations of nutrients are very specific, since individual members within a group vary manifold in toxicity (Simon-Sylvestre and Fournier 1979). In the present experiment, an attempt has been made to study the influence of phorate (O,O-diethyl-S-ethylthiomethyl-dithiophosphate) and carbofuran (2,3-dilydro-2,2-dimethyl benzofuran-7-yl-methylcarbamate) at their field rates on the mineralization and avialability of C, N and P in alluvial soil. The persistence of the insecticidal residues in soil was also studied.

MATERIALS AND METHODS

Two systemic granular insecticides, viz. phorate (10G) and carbofuran (3G)@ 1.5 and 1.0 kg a.i. ha^{-1} respectively, were mixed thoroughly with 1kg air dried and sieved (≤ 2 mm) alluvial soil (*Typic Fluvaquent*) collected from the top soil layer (0-10 cm) of the farm of Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, Nadia, India and having the general characteristics as : water holding capacity (%) 50.5, pH (1:2.5 in water) 7.3, CEC [cmol (p^{+}) k g^{-1}] 8.77, organic C (g kg^{-1}) 5.85, total N (g kg^{-1}) 0.57, NH_4^+- N

Correspondence to: A. C. Das

(mg kg^{-1}) 54.2, NO_3^-- N (mg kg^{-1}) 16.2, available P (mg kg^{-1}) 5.75, sand (%) 66.6, silt (%) 25.0 and clay (%) 8.4. After mixing insecticides, the soils were placed separately in earthenware pots adjusting water content to 60% of water holding capacity. To avoid photodegradation of insecticides, the pots were covered with black polyethylene sheet and were incubated in dark at 30°C ± l°C for 60 days. All the treatments were replicated thrice. After the incubation period of 0(lhr), 15, 30, 45 and 60 days, soil samples were collected from the replicated pots of each treatment and were analysed for organic C, total and inorganic N following the methods as outlined by Jackson (1973). Available P was estimated in $NaHCO_3$ extract (Olsen et al. 1954) calorimetrically (Jackson 1973).

The soils were also analyzed for the presence of residues of the insecticides by drawing samples after 0(1 hr), 5, 10, 15, 30, 45 and 60 days of incubation. To analyse the residues of phorate, 50 g soil sample was extracted with 100 mL chloroform in a soxhlet extraction apparatus. The extract was then concentrated to 10 mL in a Kuderna-Danish evaporator and was cleaned through a glass column (28 cm x 2 cm) containing a 5 cm layer of anlydrous Na_2SO_4 overlaid with 5g absorbent mixture of charcoal, celite and MgO (2:2:1) activated before use at 110°C for 2 to 3 hours. Residual phorate in the extract was estimated calorimetrically (Getz and Watts 1964) as modified by Jain et al. (1974). The recovery rate of phorate in soil sample was fixed at 87%.

To analyze carbofuran resudues, 50 g soil sample was extracted with 100 mL acetone in a soxhlet extraction apparatus. The extract was then partitioned with NaCl-saturated water and chloroform thrice according to the procedure of Meher et al. (1985) followed by cleaning with a glass column (30 cm x 2 cm) containing a layer of anhydrous Na_2SO_4 overlaid with a 5 cm layer of absorbent mixture of charcoal and celite (1:1) activated before use at 110 °C for 2 to 3 hours. The extract was evaporated to dryness and was taken up in 2mL acetone. Carbofuran was hydrolysed with strong alkali. The liberated phenol was coupled with 1-fluoro-2,4-dinitrobenzene and was analysed by GLC (Holden 1973) using a gas chromatograph of Tracor MT 200 model equipped with Ni^{63} electron capture detector. The aliquot of the extract was injected in a glass column (180 cm x 6.34 mm) packed with 3% OV-17 stationary phase on 80-100 mesh chromosorb-W(HP). The temperatures of injector, column and detector were maintained at 275 °C, 225 °C and 250 °C, respectively. The flow rate of carrier gas (N_2) was adjusted to 60 mL min^{-1}. The recovery rate of carbofuran in soil sample was fixed at 90%. For each insecticide, the residue values were processed to calculate the half-life ($T_{½}$) following the method of Hoskins (1961).

RESULTS AND DISCUSSION

Organic C content of the soil, in general, decreased gradually with time (Table 1) due to the utilization of carbonaceous materials by the increased microbial biomass resulting in a greater breakdown of organic matter with a subsequent loss of CO_2 from soil (Debnath et al. 1994). In accordance with the earlier report (Murthy et al. 1991), application of insecticides, particularly phorate, enhanced the mineralization of organic C in soil. A similar trend was recorded for total N content (Table I), manifesting denitrification following an enhanced micobial mineralization of organic N in soil. The stimulating influence of the insecticides on microbial mineralization of organic N (Singh and Prasad 1991) brought about a significant reduction of total N content, which was more prouounced with phorate (17.9%) followed by carbofuran (14%).

Table 1. Influence of insecticides on organic C and total N content in soil

Incubation days	Treatments		
	Control	Phorate	Carbofuran
	Amount of organic C (g kg^{-1} soil)		
0(1 hr)	5.78±0.07	5.76±0.04	5.80±0.02
15	5.65±0.04	5.47±0.11	5.62±0.04
30	5.62±0.22	5.47±0.11	5.58±0.11
45	5.55±0.04	5.40±0.11	5.47±0.07
60	5.54±0.29	5.33±0.04	5.43±0.06
	Amount of total N (g kg^{-1} soil)		
0(1 hr)	0.57±0.02	0.56±0.01	0.57±0.04
15	0.54±0.01	0.54±0.01	0.55±0.02
30	0.53±0.01	0.50±0.02	0.52±0.01
45	0.52±0.03	0.49±0.03	0.52±0.02
60	0.52±0.02	0.46±0.01	0.49±0.03

Means ± SD

The greater mineralization of N following the application of insecticides resulted greater increase in the amounts of NH_4^+-N and $N O_3^-$-N in soil (Table 2), the increment being more prounced for $N H_4^+$-N with phorate and carbofuran up to 15 and 30 days, respectively while both the insecticides recorded an incessant rise in $N O_3^-$-N up to the end of the experiment. This indicated that the insecticides probably stimulated the growth and activities of both ammonifying and nitrifying microorganisms which, in turn, released

Table 2. Influence of insecticides on inorganic N and available P content in soil

Incubation days	Treatments		
	Control	Phorate	Carbofuran
	Amount of NH_4^+-N (mg kg^{-1} soil)		
0(1 hr)	53.8±2.0	52.5±4.3	51.1±2.7
15	52.5±1.4	61.9±8.1	55.2±4.1
30	47.1±2.5	60.5±4.1	55.7±0.6
45	43.6±5.4	57.8±1.4	48.1±0.8
60	43.0±4.6	53.8±2.7	45.5±1.3
	Amount of NO_3^- -N (mg kg^{-1} soil)		
0(1 hr)	17.1±1.7	18.8±2.2	16.1±2.1
15	20.2±1.6	25.6±1.4	21.5±3.2
30	21.5±3.2	29.6±5.4	24.2±1.8
45	22.9±1.3	28.9±3.2	25.6±1.4
60	25.6±2.1	31.0±1.4	27.5±3.2
	Amount of avilable P (mg kg^{-1} soil)		
0(1 hr)	5.36±0.19	5.77±0.39	5.38±0.39
15	5.38±0.29	6.53±0.77	6.27±0.12
30	5.22±0.16	7.07±0.14	6.92±0.77
45	5.96±0.18	7.76±0.76	7.30±0.52
60	5.49±0.48	7.26±0.27	6.99±0.32

Means ± SD

larger amounts of mineral N into the soil (Das and Mukherjee 1994). In general, soil retained higher amounts of NH_4^+-N than NO_3^--N, indicating that the process of ammonification was faster than that of nitrification. Between the two insecticides, phorate released more amounts of mineral N than carbofuran did. Incorporation of insecticides also brought about a significant rise in the availability of soluble P due to the greater stimulation of the activities of phosphate solubilizing/mineralizing microorganisms (Arora and Gaur 1979) in soil. Between the two insecticides, phorate liberated more amount of available P as compared to carbofuran.

The persistence of the insecticides residues in soil varied (Table 3). Between the two insecticides, the rate of dissipation of carbofuran residues was faster than that of phorate, depicting the half-lives ($T_{½}$) 8.8 and 11.5 days, respectively. This corroborates the findings of Sahu and Agnihotri (1983), and Das et al. (1995) who also recorded the $T_{½}$ of the said insecticides 8.6 and 16.4 days, respectively. As microbial degradation is the main cause of dissipation of insecticides in soil (Rache and Coats 1988), the results pointed out that the soil microorganisms might have utilized

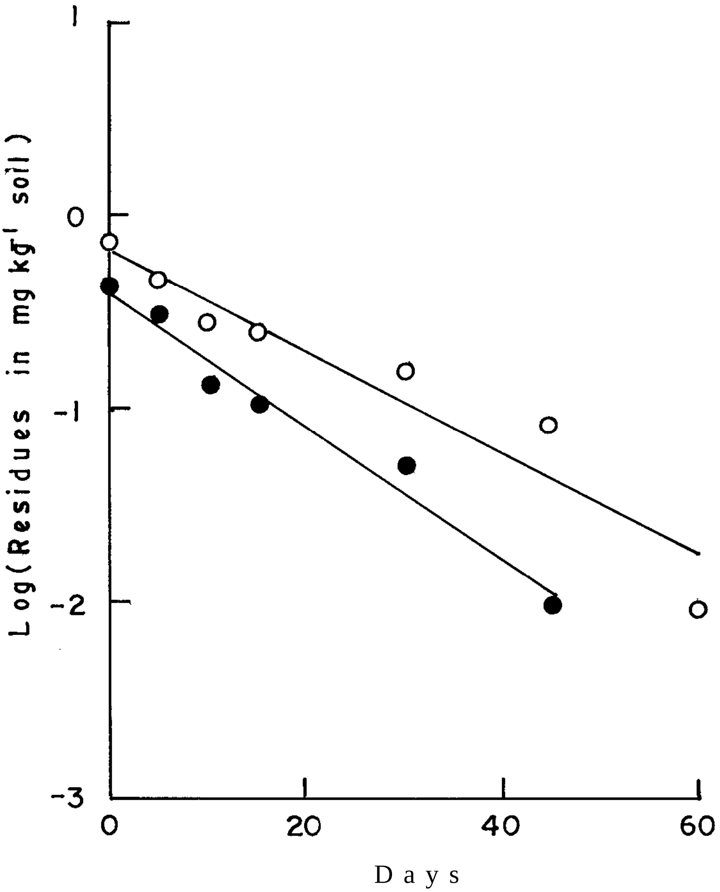

Figure 1. Linear regression of first order reaction kinetics of phorate (o --- o) and carbofuran (● --- ●) residues in soil

Table 3. Persistence of insecticidal residues in soil

Incubation days	Phorate		Carbofuran	
	Residues (mg kg^{-1} soil)	Dissipation (%)	Residues (mg kg^{-1} soil)	Dissipation (%)
0 (1 hr)	0.71±0.02	-	0.43±0.02	-
5	0.47±0.02	33.8	0.31±0.04	27.9
10	0.28±0.02	60.6	0.13±0.02	69.7
15	0.25±0.01	64.8	0.11±0.01	74.4
30	0.16±0.02	77.5	0.05±0.01	88.4
45	0.09±0.01	87.3	0.01±0.003	97.7
60	0.01±0.002	98.6	ND	-
DL	0.002		0.01	
$T_{1/2}$	11.5 days		8.8 days	
r	-0.954		-0.986	

Means ± SD, ND = Not detected, DL = detection limit, $T_{1/2}$ = half-life, r = correlation coefficient the insecticides as well as their degraded products for their growth and metabolism (Bollag 1982). It was also revealed that the rate of dissipation of both the insecticides were very rapid during early days and no residues of carbofuran was detected after 45 days of incubation. The degradation of both the insecticides in soil followed first order reaction kinetics (Fig. 1) which was also evident from significant correlation coefficient (r).

The results of the present investigation thus indicated that phorate and carbofuran were not only less persistent in soil but also stimulated the microbial mineralization of nutrient elements, which in turn, released more amounts of available nutrients in soil.

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