Indian Journal of Agricultural Sciences **81** (6): 578–81, June 2011

Sorption, degradation and movement of three carbamate pesticides in soils*

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Received: 6 August 2009; Revised accepted: 24 February 2011

Key words: Degradation, Mobility Carbamate pesticides, Sorption, Soils

Pesticides degradation and adsorption in soils are key processes to determine whether pesticides use will have any impact on environmental quality. Pesticide degradation in soil generally results in reduction of toxicity but some pesticides breakdown into more toxic compound (Villaverde *et al.* 2008). Sorption is one of the most important factors which affect transport and transformation processes of pesticides and their bioavailability. The extent of sorption depends on soil organic matter, type and contents of clay, *p*H, CEC as well as on physico-chemical properties of pesticides itself (Ertli *et al.* 2004). Besides these, microbial degradation also contributes to the transformation of carbamate pesticides.

This study was designed to determine the persistence, sorption and movement of three polar carbamate pesticides, Oxamyl (I); S-Ethyl-N- (methyl carbamoyl) oxythioactimidate (II) and N-Phenyl (ethyl carbamoyl) propylcarbmate (III) in six soils differing significantly in organic matter and other physical and chemical properties.

The six soil samples (S_1 to S_6) (0–30 cm depth) from cultivated lands of different parts of India (Bangalore, Aligarh, Kota, Jhansi, Doiawala, Ludhiana) (differing significantly in organic matter and other physico-chemical properties) were selected. The soil samples were air-dried at room temperature, sieved to pass through 2 mm sieve. The physico-chemical properties, determined by the usual soil laboratory methodology are given in Table 1.

Sorption experiments were conducted by placing 5g of air-dried soil samples in large number of glass stoppered tubes and adding various amounts of studied pesticide solution (0–15 ml of 100 µg/ml in 0.01 M $CaCl_2$ at a constant ionic strength) and making up to 25 mL with distilled water. The suspensions were shaken for 30 hr at 20±2°C (preliminary studies indicated that equilibrium was attained in < 27 hr), followed by centrifugation at 13 000 rpm for 10 min. The amount of pesticides in supernatants was estimated as discussed elsewhere (Bansal 2004).

For persistence and degradation studies 2 kg of soil were incubated with 0, 10, 20, 50 and 100 µg/g soils of three carbamate pesticides in several polypropylene pots separately at 80% of water retention capacity. Moisture was regularly maintained based on the difference in between two consecutive days. Samples were incubated at 20±1°C. The residues were monitored at the time interval of 0 (4 hr), 7, 14, 21, 28, 35, 42, 49, 56, 63, 70, 77, 84 and 91 days after incubation followed by residue analysis.

The mobility studies were conducted in 60 cm×12 cm PVC pipes. The lower end of pipes was sealed with polyethylene and cotton cloth. The pipes were filled with 10 kg of each soil and 500 mg of pesticides (50 mg/kg soils) were applied separately in each pipe at 80% of water retention capacity. Soil samples were collected using a steel soil

Table 1 Selected physical and chemical properties of the soils used

Soil	Location	Organic matter (%)	Organic carbon (g/kg soil)	Clay (%)	Sand (%)	Silt (%)	*p*H (1:2.5)	CEC [cmol (p+)/kg]
S_1	Bangalore	1.24	7.2	19.4	30.4	50.2	6.4	6.5
S_2	Aligarh	1.75	10.1	13.4	38.4	48.2	8.8	11.4
S_3	Kota	3.40	19.7	46.2	11.2	42.6	7.2	30.6
S_4	Jhansi	1.48	9.6	28.2	47.2	24.6	7.5	23.7
S_5	Doiawala	2.30	13.3	20.6	25.2	54.2	5.9	19.5
S_6	Ludhiana	0.78	4.5	30.2	31.2	38.6	8.4	15.2

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sampler at the depth of 0–15 and 15–30 cm after 0, 7, 14, 21, 28, 35, 42, 49 days of application and at the depth of 0–15, 15–30, 30–45, 45–60 cm after 56, 63, 70, 77 and 91 days of application, followed by residue analysis. All the experiments were done in triplicate with suitable blanks.

Simple and multiple linear regression analysis and the correlation between sorption and soil properties were obtained using origin 5.0 (Microcal Software, Inc.).

All the sorption isotherms (Fig 1) displayed small non-linearity and were described satisfactorily by the Freundlich equation with the correlation coefficient (R^2) > 0.98 (Table 2). The values of 1/n during the sorption studies were < 1 indicating a convex or L type of isotherms (Giles *et al.* 1974). This kind of isotherms may arise because of minimum competition of solvent for sites on the adsorbing surface. The L shape of isotherms is indicative of a gradual decrease in the sites available for sorption as the concentration of solute in the solution increased. L shape of isotherms for sorption may be due to specific interactions between pesticide and soil surface via charge transfer, dipole-dipole attraction, hydrogen bonding, and/or protonation. The lack of linearity (1/n <1) also supports the view that sorption is governed by other factors in addition of simple partition in organic phase (Stipicenic *et al*. 2009). The values of 1/n also suggest that the pesticide molecules are likely to be sorbed in a flat position (Giles *et al.* 1974). The values of K_f and 1/n were in the order pesticide III > I > II. The K_f values and adsorption of studied carbamate pesticides decreased in the order $S_3 > S_5 > S_2 > S_4 > S_1 > S_6$.

The correlation between sorption and soil properties can be used to elucidate the factors of soil dominating in the sorption process. Multiple linear regressions resulted in the following correlation between K_f and soil properties for pesticides I, II, III respectively.

K_f = -4.895 + 9.084 W_{OM} + 0.1183 *p*H + 0.0068 W clay + 0.0730 CEC (R^2=0.976) … (i)

K_f = -1.062 + 5.4346 W_{OM} + 0.00058 *p*H + 0.1073 W clay + 0.0268 CEC (R^2 = 0.982) (ii)

K_f = -5.14 + 9.799 W_{OM} + 0.0356 *p*H – 0.0620 W clay + 0.2755 CEC) (R^2= 0.972) (iii)

These results suggest that organic matter contributed predominately (Cox *et al.* 1998) to the sorption of carbamate pesticides on the soils studied and order of sorption was pesticide III > I > II. The values of simple linear regression coefficients showed that K_f and clay content were also positively correlated (was R^2 = 0.48–0.52) indicating that the clay content was the other soil property influencing the sorption of pesticides on soils. The K_{om} values ($K_{om} = K_f$/OM%×100) suggest that other soil properties have smaller influence on the sorption of studied pesticides on soils. The heat released during the carbamate pesticides sorption on studied soils ranged between 15.26 and 16.87 kJ/mole. The low heat of sorption (< 50 kJ/mole) indicates that the sorption of pesticides was primarily via physical process (Hulscher

Table 2 Freundlich parameters for three carbamate pesticides adsorption in soils

Property	Soils																	
	S_1			S_2			S_3			S_4			S_5			S_6		
	Pesticides																	
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
K_f	8.1	7.2	8.9	13.0	12.0	14.3	29.5	24.2	34.5	10.6	9.3	12.4	18.2	15.3	21.6	4.8	4.1	5.8
1/n	0.772	0.756	0.792	0.802	0.784	0.832	0.856	0.820	0.912	0.784	0.772	0.810	0.814	0.800	0.884	0.764	0.750	0.782
R^2	0.982	0.974	0.992	0.988	0.980	0.996	0.968	0.984	0.992	0.982	0.981	0.988	0.990	0.984	0.986	0.988	0.990	0.976
K_{om}	653.2	580.6	717.7	742.8	685.7	817.6	867.6	711.7	1014.7	716.2	628.4	837.8	791.3	665.2	939.1	615.4	525.6	743.6
ΔG (kJ/mole)	−15.8	−15.5	−16.0	−16.1	−15.9	−16.3	−16.5	−16.0	−16.9	−16.0	−15.7	−16.4	−16.2	−15.8	−16.7	−15.7	−15.3	−16.1

and Cornelissen 1996), ie charge transfer, hydrogen bonding, protonation, cationic adsorption with or with out water bridge into soil organic matter. These findings were in good agreement with the results of Bansal (2004).

The dissipation half lives (DT_{50}) were calculated using a first order dissipation model Equation (1) describes the dissipation kinetics and equation (2) is used to calculate dissipation half lives $C_t = Co \times e^{-(kt)}$ ….. (1) $DT_{50} = 0.693/k$ ….. (2)

Where, Co and C_t are the concentration of analyses at time 0 and time t (days) respectively, k is the first order rate constant determined as the slope value from test substance dissipation curves, as the regression lines generated have a coefficient of determination $R^2 > 0.95$. Similar results have also been reported by other workers for various pesticides (Hu and Coates 2008). Data on k and DT_{50} showed that the rate of degradation followed the soil in the order $S_6 > S_2 > S_4 > S_1 > S_5 > S_3$ indicating, thereby a role of soil organic matter, clay content and soil *p*H. The rate of degradation is related inversely to the order of sorption as soil S_3 has maximum sorption and minimum degradation. Soils rich in OM may retain the pesticide and reduces dissipation and possibility of contaminating the surface and groundwater. The DT_{50} (50% dissipated) for three carbamate pesticides was in the order II > I > III denoting that pesticide III is most stable, followed by I and II. The values of DT_{50} ranged from 35.4 to 50.9 d for pesticide I; 33.3 to 45.6 d for pesticide II and 38.1 to 56.8 d for pesticide III. The values of DT_{50} were significantly positively correlated with OM ($R^2 = 0.87$–0.92) and clay content ($R^2 = 0.48$–0.52), while non- significantly negatively correlated with soil *p*H ($R^2 = -0.30$– 0.27). The values of correlation coefficients showed clay content was the second major soil property influencing the sorption of carbamate pesticides on soils. Non-significant negative correlation between *p*H and DT_{50} was possibly owing to rapid hydrolysis with increase of *p*H from 5.9 to 8.8. From the data of DT_{50} it may be inferred that there is a fairly similar microbial activity in the studied soils.

Results of mobility studies denote that the studied carbamate pesticides in all the tested soils did not leach below 45 cm. The concentration of studied carbamate pesticides below 15 cm after 91 days of application was 30–45% of the

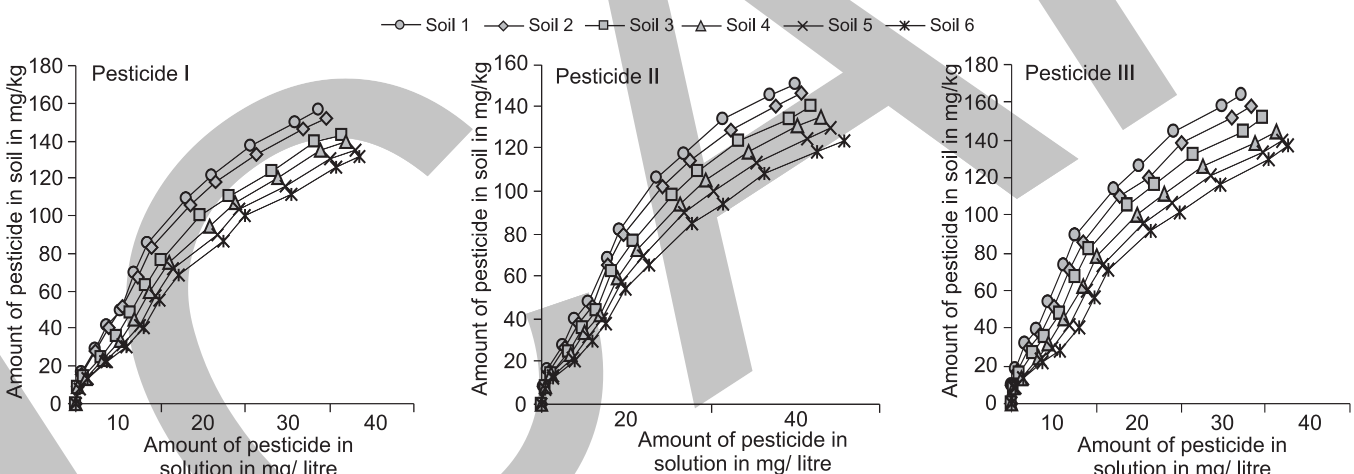

Fig 1 Sorption isotherms for carbamate pesticides on different soils

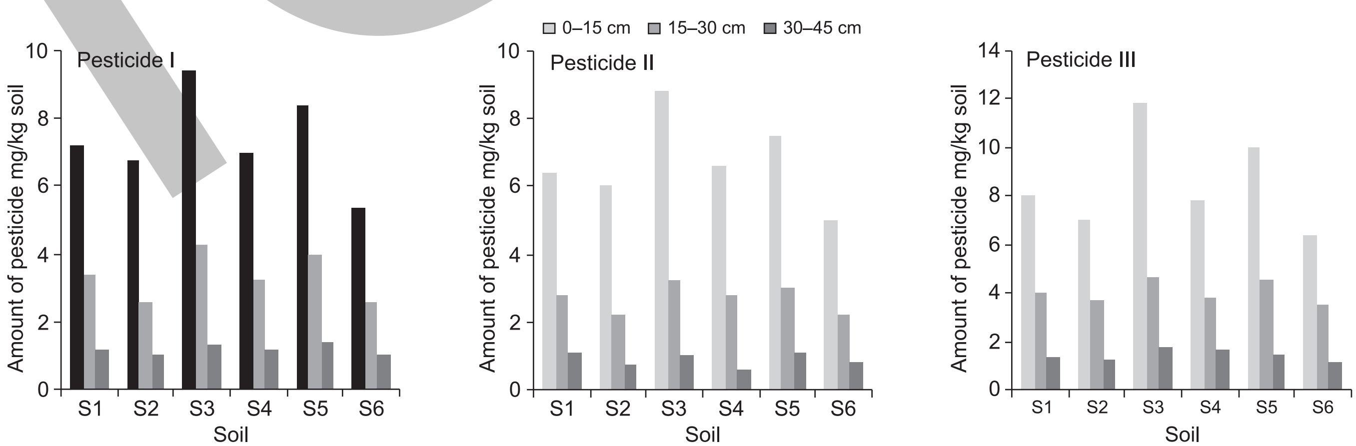

Fig 2 Distribution of carbamate pesticides in soil profile after 91 DAT

initial amount of herbicide applied. The leaching of pesticides was in the order soil $S_6 > S_2 > S_4 > S_1 > S_5 > S_3$ (Fig 2). The amount of pesticide leached below 15 cm depth showed a strong inverse relationship to sorption and soil organic matter.

SUMMARY

A study was conducted during January 2009 to May 2009 to determine the persistence, sorption and mobility of three carbamate pesticides in six different soils varying significantly in organic matter and other physical and chemical properties. The sorption of three carbamate pesticides on all the tested soils belongs to 'L type'. Sorption increased with increasing soil organic matter content but was not significantly correlated with other soil properties. These results indicate that soil organic matter was the primary site for sorption. The value of heat of sorption calculated from K_{om} suggests that partition into soil organic matter is the probable mechanism. The process of degradation followed the first order process. DT_{50} value ranged from 33.3±2.0 to 56.8±3.2 days. The degradation was rapid in alkaline medium than in neutral or acidic medium. The degradation was inversely correlated with soil organic matter. The degradation was in the order pesticide II > I > III. The mobility of pesticides in soils was up to 45 cm. Mobility below 15 cm after 91 days of application was 30–45% of initial amount. The relatively strong and quick soil adsorption of these pesticides could be accounted for its limited leaching. These results indicate that the studied carbamate pesticide pose a considerable environmental risk owing to its short $DT_{50,}$ reduced soil residues and limited leaching

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