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INFLUENCE OF TEMPERATURE, ORGANIC MATTER AND pH ON ADSORPTION OF DIMETHOATE BY SOILS AND CLAYS*

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Effect of temperature, organic matter and pH on adsorption of dimethoate by clays and soils were investigated. Adsorption of dimethoate decreased as temperature increased on both Ca-montmorillonite and Ca-Kaolinite. Among clays Ca-Montmorillonite was superior over Ca-Kaolinite. The values of change in free energies (ΔG) indicated that Vander Waal's forces were prominent in adsorption. Adsorption of dimethoate was highest in activated soil and least in soils where organic matter was removed by H_2O_2 pre-treatment. Differences in K values of various treatments suggest that organic matter played a dominant role in the adsorbent of this insecticide.

Adsorption of dimethoate was a function of pH and it was highest in all soils when pH was 5.0 and it was lowest when pH of soil was 8.6. It is postulated that adsorption was by physical means when pH remained 7 and above and by protonation and ion-exchange under acidic soil environment.

A great deal of attention has been paid in recent past to investigate adsorption behaviour of pesticides, particularly the organophosphates by soils and clay minerals. Dimethoate (0, 0-dimethyl S-(N-methyl carbomoyl methyl) phosporodithionate) is extensively used as a systemic insecticide. The adsorption-desorption patterns of dimethoate in relation to various physico-chemical characteristics of adsorbents largely determines the amount of pesticice available for biological action. As for dimethoate, the temperature, pH, organic matter and the type and amount of clay. (El Beit *et al.*, 1968, and Sahu and Patnaik, 1978) have been reported to be important in adsorption process. Information on adsorption of this insecticide in varied soil environmental conditions of tropics and subtropics is still lacking. Hence, the present study was initiated to relate adsorption behaviour of dimethoate as a function of clay type, temperature, organic matter and pH of the adsorbents.

MATERIALS AND METHOD

The technical grade of dimethoate (97-99 per cent) was supplied by M/s. Rallis India Limited (R & D), Bangalore. All solvents used in extraction were of analar grade. Three soil samples viz. Red sandy loam from Bangalore, Black clay soil from Dharwad and Laterite, Sandy clay loam from Coorg were collected for the study. The physico-chemical characteristics of the soils used are :

i) Red, sandy loam (Rhodustalf), pH 6.6, Org. carbon 0.51 per cent, clay 14.8 per cent, CEC 14.2 me/100 g and surface area 28.51 m^2/g.

ii) Laterite, sandy clay loam (Haplustox), pH 5.8, Organic carbon 0.6

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per cent, clay 27.6 per cent, CEC 21.3 me/100 g and surface area 36.3 m^2/g.

iii) Black clay soil (Grumaquert). pH 8.1, Org. carbon 0.48 per cent, clay 56.6 per cent, CEC 69.9 me/100 g and surface area 763.3 m^2/g.

Adsorption experiments :

i) Effect of temperature on adsorption

Adsorption as function of temperature and clay type was studied on homoionic montmorillonite and kaolinite clays, Clays were made himoionic with Ca. The homoionic clays weighing 0.1 g were transferred into 50 ml glass centrifuge tubes. Twenty ml of 0.002 *M* $CaCl_2$ having graded amounts (ranging from 200-600 μg/g) were added. The suspensions were allowed to equilibrate for 8 hrs at 18, 25 and 37°C in incubator. On the following day, suspensions were shaken for 2 hrs and centrifuged at 2000 rpm for 5 min to collect supernatant. The supernatant was subsequently used for extraction and estimation of dimethoate.

ii) Effect of organic matter on adsorption

Soils selected were a) activated soil, b) organic matter-free soil and c) natural soil. Soils were activated at 108°C for 6 hrs and cooled in descicator and used. The second category included soils from which the organic matter was oxidized with H_2O_2 as described by Felsot and Dahm (1979). Soils without any treatment served as natural soil.

To 2 g each of the three types of soils, solution of 0.002 *M* $CaCl_2$ containing dimethoate ranging from 10-30 μg/g. were added to equilibrate for 2 hrs by shaking. The soil suspensions were centrifuged at 2000 rpm for 5 min. The centrifugate was analysed for dimethoate.

iii) Effect of pH on adsorption

The measurement of adsorption as a function of pH were performed by adjusting pH of soil suspensions containing dimethoate by adding either dil. HCl or NaOH. The equilibration and other details remained same as mentioned in above paragraph.

Insecticide extraction and analysis

Aliquotes of the centrifugate of different experiments were extracted with chloroform (3 x 30 ml) as per method described by EL. Beit *et al.* (1968). The pooled extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue left was redissolved in 5 ml of acetone No clean up of the residues were found necessary in this experiment. The amount of dimethoate was computed by injecting 2 μl of sample containing p-nitrophenol as internal standard into Varian GC 3700 with TSD as detector. The operating conditions were :

Column : 50 cm s. s. packed with 5 per cent OV-101 on chromosorb WP 80-100 mesh.

Temp : Column- 180°C, Inj. Port-224°C Detector-220°C.

Gas flow : Nitrogen-30 ml/min, Air-150 ml/min, Hydrogen-4 ml/min.

Polarity : Positive, Bias voltage - 4V, Bead current - 5.44 A

Chart speed : 1 cm/min and Retention time - Dimethoate 0.8 min - PNP - 0.4 min.

The peak heights of internal standard and dimethoate were measured to compute amount of dimethoate as described by Lee and Westcott (1979). The data obtained on the amount of dimethoate adsorbed and that which remained in equilibrium solution were transformed to log form of the empirical Freundlich's equation to find out k and n values.

RESULTS AND DISCUSSION

Effect of temperature and clay type

Results showing the effect of temperature and clay type are presented in Table 1. Adsorption of dimethoate decreased as equilibration temperature increased since adsorption is an exothermic in nature. Adsorption of dimethoate was high on Ca-montmorillonite than Ca-kaolinite. The decrease in adsorption with increase in temperature may correspond to the increased tendency of solute to escape from adsorbed surface and increased solubility of pesticide. Similar decrease in adsorption with temperature (Goring, 1967; Bailey and White, 1970; Yaron and Saltzman. 1972, Bigger *et al*, 1978 and Kausalya *et al.*, 1982) have been reported to be due to the decreased attractive forces between adsorbent and adsorbate. The results of this experiment are in agreement with the findings of workers cited earlier.

Table 1. Influence of temperature on adsorption of dimethoate by clays

Quantity of pesticide added (μg/g)	Ca-Montmorillonite 18±1°C Q. A*	k	n	25±1°C Q. A	k	n	37±1°C Q. A,	k	n	Ca-Kaolinite 18±1°C Q. A.	k	n	25±1°C Q. A.	k	n	37±1°C Q. A.	k	n
200	176.29 (88.15)**			162.20 (81.10)			140.37 (70.19)			162.42 (81.21)			143.77 (71.89)			133.17 (66.59)		
800	254.88 (84.96)			236.90 (78.97)			207.75 (69.25)			248.12 (82.71)			203.34 (67.75)			198.69 (66.23)		
400	337.50 (84.38)			298.50 (74.45)			282.77 (70.70)			303.85 (75.97)			279.75 (69.94)			273.50 (68.38)		
500	424.75 (84.95)			362.50 (72.50)			326.19 (65.24)			390.75 (78.15)			343.50 (68.70)			311.60 (62.32)		
600	480.00 (80.00)			409.79 (68.30)			390.70 (65.12)			459.19 (76.54)			388.87 (64.42)			352.60 (58.77)		
		19:95	1.43		7.78	1.63		11.89	12.6		9.34	1.38		7.94	1.30		7.08	1.38
$-\Delta G$ (K Cal. Mol)	- 1.78			—1.71			—1.47			—1.33			—1.23			—1.16		

**Figures in parentheses are per cent adsorbed

*Quantity Adsorbed (μg/g)

Effect of clay type and temperature	S.Em±	CD at 0.05%
Between quantities added	6.10	17.99
Between clay types	3.86	11.39
Between temperature	4.73	13.96
Clay type + temperature	6.68	19.70

The values of Freundlich's constant k also decreased with increase in temperature, the values of k was higher for Ca-montmorillonite than Ca-kaolinite indicating superiority of former adsorbent. The values of change in free energies (ΔG) were negative indicating spontaneous adsorption of this insecticide. Since the values of ΔG were lower than those reported for chemisorption by Hamakar and Thomson (1972), it is reasoned that the adsorption mechanism was through Vander Waal's forces.

Effect of organic matter

From the foregoing results (Table 2), it is clear that adsorption of dimethoate was high in all activated soils and least in organic matter-free soils. On destruction of organic matter from soils (with H_2O_2) adsorption diminished and the extent of reduction varied from 25-35 per cent suggesting the importance of organic matter in adsorption However, the adsorption of this insecticide in natural soil remained intermediate between other treatments in all the soils studied. Activation of soils usually removes water and air exposing more specific surface area for adsorption. The increased surface area on activation resulted in higher adsorption of dimethoate. The results of similar trend have been reported by several workers including Wahid and Sethunathan (1978) and Sethi

Table 2. Influence of organic matter on adsorption of dimethoate by soils

Quantity added (ug/g)	Quantity adsorbed (μg/g)								
	Black			Red			Leterite		
	Activated	Natural	OM-free	Activated	Natural	OM-free	Activated	Natural	OM-free
10	8.91 [89.10]*	8.72 [87.20]	8.05 [80.50]	8.34 [83.40]	6.50 [65.00]	5.50 [55.00]	8.10 [81.00]	7.49 [74.30]	4.33 [43.30]
15	13.75 [91.67]	12.92 [86.14]	10.33 [68.87]	11.67 [77.80]	9.60 [64.00]	6.40 [47.67]	10.89 [72.60]	8.17 [54.47]	6.32 [42.14]
20	18.33 [91.65]	16.67 [83.35]	12.05 [60.25]	13.66 [68.30]	11.21 [56.05]	7.33 [36.65]	14.75 [73.75]	10.50 [52.50]	7.30 [36.50]
25	21.25 [85.00]	20.09 [82.76]	13.33 [53.32]	14.05 [56.29]	12.67 [50.68]	8.50 [34.00]	14.85 [59.40]	12.75 [51.00]	8.80 [35.20]
30	25.75 [85.84]	24.67 [82.24]	15.55 [52.84]	15.67 [52.24]	13.37 [44.67]	9.11 [30.37]	17.20 [57.34]	13.00 [43.34]	10.40 [34.67]

Figures in the parenthesis are per cent adsorbed

Effect of organic matter and soil type on adsorption

	S. Em±	CD at 0.05%
Between quantities added	0.64	1.77
Between treatments imposed	0.50	1.39
Between soil types	0.50	1.39
Treatments to soil x soil type	0.86	2.38

and chopra (1975). Even though the magnitude of adsorption decreased on account of removal of organic matter by oxidation with H_2O_2 the adsorption was around 80 per cent in case of black soil and the high adsorption could be attributed to the involvement of other factors during the adsorption of dimethoate. The higher adsorption of dimethoate by organic matter free black soils can be related to the clay content. Similar views on the involvement of clay have been reported by several workers including Sahu and Patnaik (1978) and Saltzman *et al.* (1972).

The values of k (Table 4) also diminished on removal of organic matter from soils. The values remained highest in activated soil followed by natural and organic matter-free soils, respectively. The variable (n) values of slope obtained as a measure of energies of adsorption suggested the complex nature of adsorption involving different adsorption sites and surface energies (Felsot and Dahm 1979).

Effect of PH

Results on the effect of pH on adsorption of dimethoate are presented in Table 3. Over pH range studied, it was noticed that adsorption significantly decreased with increase in pH to 8.6 in all soils studied. Adsorption of dimethoate was found to be highest, in all soils when pH of soil suspension was 5.0 while the lowest value was obtained at pH 8.6. The reduction in adsorption on account of increase in pH was 63.4 per cent in black and around 32.0 per cent in other soils types. In view of higher adsorption at lower pH, it is postulated that highe

Table 3. Influence of pH on adsorption of dimethoate by soils

Quantity added	Quantity adsorbed [μg/g]								
	Black			Red			Laterite		
[μg/g]	5.0	7.0	8.2	5.0	7.8	8.2	5.0	7.0	8.2
10	8.85 [88.50]*	7.92 [79.20]	5.83 [58.30]	7.02 [70.20]	5.75 [57.50]	3.75 [37.50]	7.25 [62.50]	6.24 [72.40]	3.27 [32.70]
15	13.67 [91.14]	10.42 [69.47]	5.88 [39.20]	9.53 [63.67]	6.67 [44.47]	5.65 [37.67]	9.77 [65.40]	7.25 [48.34]	5.73 [38.20]
20	17.88 [89.40]	12.50 [62.50]	6.25 [31.25]	11.80 (59.00]	7.50 [37.50]	7.33 [36.65]	11.88 [59.40]	9.67 [48.35]	6.74 [33.70]
25	22.42 [89.68]	14.58 [58.32]	6.67 [26.68]	12.75 [57.00]	9.44 [37.76]	8.95 [35.88]	13.33 [53.32]	11.33 [45.32]	8.81 [35.24]
30	26.75 [89.17]	15.83 [52.77]	8.33 [27.77]	16.84 [56.74]	11.39 [37.97]	9.77 [32.77]	17.98 [59.94]	13.79 [45.97]	9.67 [32.24]

Figures in parenthesis are per cent adsorbed

Effect of pH and soil type on adsorption

	S. Em±	CD at 0.5%
Between quantities added	0.80	2.22
Between soil types	0.63	1.74
Between pH	0.63	1.74
Soil type x pH	1.08	2.99

Table 4. Relationship of pH and Organic matter Versus Freundlich constants for the adsorption of Dimethoate by soil.

Soil type	Organic matter						pH					
	Activated		Natural		Organic matter-free		5.0		7.0		8.6	
	k	n	k	n	k	n	k	n	k	n	k	n
Black	10.47	2.25	8.32	2.00	7.59	1.80	13.18	1.03	6.03	2.60	2.19	2.50
Red	8.13	2.80	3.98	2.50	3.72	2.60	2.63	1.50	1.91	1.45	0.48	1.11
Laterite	5.25	2.06	2.63	1.48	1.38	1.50	4.17	1.59	2.40	1.88	0.96	1.33

adsorption was possible through protonation, followed by ion exchange reactions with the adsorbent. Dimethoate has polar P = S, C=O and terminal NH, functional groups, and is therefore readily adsorbed by soils and organic matter. The adsorption of dimethoate was low at pH values exceeding 7.0 where protonation is unlikely to be important and the dominant mechanism would be the van der Waal's forces. Both protonation and van der Waal's forces have been reported to be more pronounced in acidic range, while only van der Waal's forces operate at higher pH conditions (Bailey and White, 1970).

The lower values of K and N observed with increase in pH in all soils could be attributed to the decreased adsorption. As observed earlier the adsorption of dimethoate was pH dependent. The overall differences in the adsorption of dimethoate between soils was statistically significant. Among soils, black soils adsorbed highest amounts of dimethoate over the other soils studied due to the differences in the physicochemical characteristics of black soil.

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SEED QUALITY IN CSH 5 HYBRID SORGHUM AS INFLUNCED BY THE SPACING OF MOTHER PLANT

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Evaluation of seed quality of sorghum CSH 5 hybrid obtained from filed trials carried out both in the monsoon and winter seasons with a common interspacing of 45 cm between rows and with intra-row spacings 20, 15, 10 and 5 cm given to the mother plant (ms 2077A) revealed that 100-seed weight, germination percentage, root length and vigour index were higher for the seeds from 45 x 15 cm spacing over other spacings.

Among different pre-harvest environmental factors, spacing of mother plant plays an important role in seed quality (Austin, 1972; Aswathaiah, 1977 and Vanangamudi, 1982). Similar information on seed quality is lacking in hybrid sorghum CSH 5 and hence, studies were initiated to know the effect of spacing of the mother plant on the quality of CSH 5 hybrid seed.

MATERIALS AND METHODS

Field trials were laid out with the parental lines of CSH 5 (ms 2077 A and CS 3541) during monsoon and winter seasons adopting Randomized Block Design with six replications. An inter-row spacing of 45 cm and intra-row spacings of 20, 15, 10 and 5 cm were given to the mother parent. The

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