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The Effects of composts on adsorption-desorption of three carbamate pesticides in different soils of Aligarh district

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ABSTRACT: The effects of various organic manure [farm yield manure (FYM), sewage sludge and poultry manure] application on adsorption-desorption of three carbamate pesticides [oxamyl(I);S-Ethyl-N-methylcarbamoyl)oxy]thioacetimidate (II) and N-Phenyl (ethyl carbamoyl) propyl carbamate (III) on six soil samples of Aligarh district was studied. Addition of organic manure increased soil organic carbon content and electrical conductance while pH decreased. The results of the study denoted that adsorption isotherms were 'L' type and adsorption-desorption data conformed to Freundlich adsorption isotherm equation. The adsorption increased with the increase in organic manure and followed the order sewage sludge > FYM > poultry manure. The adsorptivity of soils was in order soil No. 1 > 2 > 3 > 4 > 5 > 6. The adsorption capacity was significantly positively correlated with soil organic carbon and CEC and negatively correlated with soil pH. Desorption was more in unamended soil than manure amended soil and decreased with the increase in amount of organic manure. Desorption showed hystersis, indicate by the higher adsorption slope (1/n ads) compared with desorption slope (1/n des). @JASEM

Pesticides adsorption and desorption are the key processes determining whether pesticide used will have any impact on environmental quality. For most of the pesticides soil organic matter and clay contents are the most important properties which affect the sorption and transformation (Durovic *et al.,* 2009; Osborn *et al.,* 2009; Villavarde *et al.,* 2008). The use of composts derived from source-separated municipal solid waste/animal manure/FYM is now a common agronomic practice throughout the world. Such amendments improve the physico-chemical properties of the soil. Application of such composts affect the fate and mobility of applied pesticides in soil as addition of compost increases besides nutrients the soil organic matter content (Paustin *et al.,* 1992). Carbamate pesticides are widely used as insecticides, nematicides and herbicides (Hague, 1979). Investigations on the adsorption of carbamate pesticides by clays have shown that they are adsorbed by co-ordination and/or protonation at the carbonyl oxygen by exchangeable cations of clays (Bansal 2009, 1983; Li *et al.,* 2003). The purpose of the present study is to study the effect of different amount of organic manure (FYM, sewage sludge and poultry manure) on the extent of adsorption/desorption of three polar water soluble carbamate pesticides; oxamyl (I) [methyl-2-(dimethylamine)-N-{(methyl amino) carbonyl}oxy]-2-oxoethanimidothioate $(CH_3)_2NCO(SCH_3)=NOCOCH_3$; S-Ethyl-N-(methylcarbamoyl)oxy]thioacetimidate (II) CH_3-NH-CO-N=C(CH_3) (SCH_3); and N-Phenyl (ethyl carbamoyl) propyl carbamate (III) ($C_6H_5NHCOOCH(CH_3)CONHC_3H_7$ in six soils of Aligarh district.

MATERIAL AND METHODS

The six soils (1-6) selected for this study were taken from different parts of Aligarh district at plough layer (0-30 cm). They were air dried at room temperature and sieved by passing through a 100 mesh sieve. Their physico-chemical properties were determined by the usual soil laboratory methodology and clay mineralogy by an X-ray diffraction procedure on orientated specimen. Physico-chemical properties, clay mineralogy and classification are given in Table 1.

Table 1. Characteristics of soils

S/No	Place	Taxonomical name	Soil units	Silt %	Clay %	pH (1:2:5)	Organic C %	$CaCO_3$ %	CEC (Cmol (P^+) kg^{-1})	Surface area m^2g^{-1}	Major clay minerals
1.	A	Entisol	Typic Ustochrept	38.8	16.2	7.8	0.88	6.3	12.8	38.6	Q,I,C
2.	B	Acidisol	Typic Arigids	52.0	14.0	8.8	0.72	7.6	11.6	36.2	Q,I,C
3.	C	Aridisol	Typic Orthids	37.5	12.0	7.4	0.63	5.8	10. 8	30.1	Q,M,I,C
4.	D	Aridisol	Typic Orthids	44.9	13.6	7.6	0.56	6.6	10.3	27.2	Q,I,C
5.	E	Aftisol	Calciorthents	24.9	9.8	8.3	0.44	8.8	9.9	32.1	Q,I,K,C
6.	*F*	*Inceptisol*	*Calciorthents*	*27.1*	*8.5*	*8.1* *7.9* *7.6* *6.9*	*0.48* *23.3* *26.6* *20.2*	*9.0*	*8.6* *42* *46* *38*	*25.6*	*Q,I,K,C*

A = Hathras; B = Sikandra Rao; C = Datawali; D Khair = ; E = Atrauli; F = Bank of Yamuna Tappal FYM Sewage sludge Poultry manure; Q = Quartz, I – Illite, M = ontmorillonite, C = Calcite, K = Kaolinite

Soil amendment **:** Soils (1-6) were amended with 0, 2.5 and 5 g of organic manure (FYM, sewage sludge and poultry manure) kg^{-1} soil at 60% moisture level of water holding capacity and incubated for 45d at the temperature 25±2°C. The physico-chemical properties of amended soils as determined by standard methods are given in Table 2.

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Table 2. Effect of application on organic material on soil properties

Organic material added g kg^{-1} soil		Soil 1			Soil 2			Soil 3			Soil 4			Soil 5			Soil 6		
		pH	OC g kg^{-1}	EC dSm^{-1}	pH	OC g kg^{-1}	EC dSm^{-1}	pH	OC g kg^{-1}	EC dSm^{-1}	pH	OC g kg^{-1}	EC dSm^{-1}	pH	OC g kg^{-1}	EC dSm^{-1}	pH	OC g kg^{-1}	EC dSm^{-1}
Sewage sludge	0	7.8	8.8	0.66	8.8	7.2	0.61	7.4	6.3	0.55	7.6	5.6	0.57	8.3	4.5	0.52	8.1	4.8	0.44
	2.5	7.7	10.6	0.73	8.5	9.9	0.67	7.3	8.9	0.59	7.4	8.1	0.59	8.1	7.0	0.56	8.0	7.5	0.49
	5.0	7.5	11.7	0.78	8.1	11.0	0.71	7.2	10.0	0.66	7.1	9.3	0.63	7.8	8.1	0.60	7.7	8.0	0.53
FYM	0	7.8	8.8	0.66	8.8	7.2	0.61	7.4	6.3	0.55	7.6	5.6	0.57	8.3	4.5	0.52	8.1	4.8	0.44
	2.5	7.7	10.3	0.71	8.5	9.7	0.68	7.4	8.7	0.57	7.4	8.0	0.58	8.1	6.9	0.55	7.9	7.2	0.48
	5.0	7.6	11.4	0.76	8.2	10.7	0.70	7.3	9.8	0.63	7.2	9.1	0.62	7.8	8.0	0.60	7.7	7.9	0.52
Poultry manure	0	7.8	8.8	0.66	8.8	7.2	0.61	7.4	6.3	0.55	7.6	5.6	0.57	8.3	4.5	0.62	8.1	4.8	0.44
	2.5	7.7	10.0	0.70	8.5	9.6	0.66	7.4	8.6	0.57	7.5	7.8	0.60	8.2	6.8	0.55	7.9	7.2	0.47
	5.0	7.7	11.0	0.73	8.2	10.5	0.69	7.2	9.6	0.62	7.2	8.9	0.61	7.9	7.8	0.58	7.8	7.8	0.50

OC = Organic carbon

Adsorption studies : Adsorption experiments were conducted taking soil samples (10 g) (unamended and amended with organic material at 60% moisture level) in a large number of stoppered conical flask adding various amounts of standard pesticide solution (0-15 mL of 2500 µg mL^{-1}) and making up the volume to 100 mL with distilled water. The suspensions were shaken for 30h at 25±2°C (preliminary studies indicated that equilibrium was attained within <27 h) followed by centrifugation.

Residue estimation **:** The supernatants were evaporated, residues(dissolved in n-hexane)were analyzed on a Perkin Elmer GC model 8700 gas chromatograph, equipped with a ^{63}Ni electron capture detector fitted with SE 54 capillary column (60 m, 0.2 mm id). The operating conditions were as follows: column temperature 260°C, injector and detector temperature 300°C. The flow rate of nitrogen gas was 50 mL min^{-1}. The retention time for carbamate pesticides I, II, III were 2.14, 1.84 and 2.62 min respectively. Before using, the GC column was primed with several injections of standard pesticides till a consistent response was obtained for each pesticide. The concentration of sample was quantified by comparing the peak height of the sample chromatograms with those of standard run under identical operating conditions. Recovery was 93-99% and minimum detection was 0.05 µg g^{-1}.

Desorption studies **:** For desorption 50 mL of distilled water was added to soil residue left in after centrifugation and samples were shaken for 30h in a shaker. Supernatant was centrifuged and amount of pesticide desorbed was estimated in aliquots as cited above.
All the experiments were conducted in duplicate with suitable blanks.

RESULTS AND DISCUSSION

Table 2 denotes that addition of organic manure (FYM, sewage sludge, poultry manure) to soil influences the soil chemical properties. Soil organic carbon content, electrical conductance increased while pH decreased.

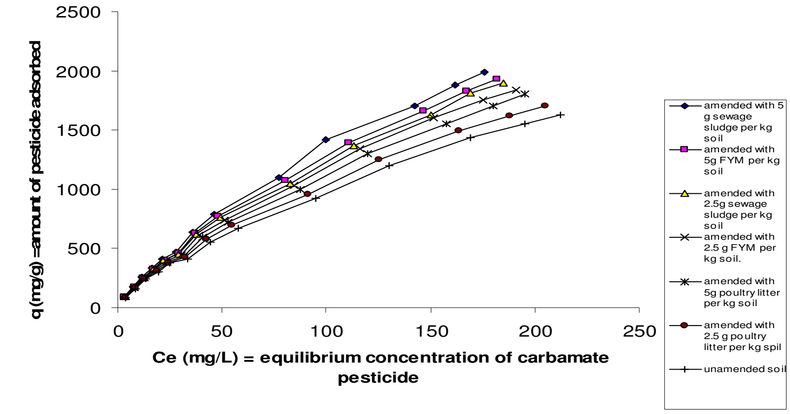

Fig 1 Effect of organic manure on the adsorption of pesticide I on soil 1.

The empirical Freundlich relationship can be used to describe carbamate pesticide adsorption results on soils of Aligarh district. The linear form of this equation is log C = log K + 1/n log Ce. Where C is the amount (mg kg^{-1}) of pesticide adsorbed by soil, Ce is the equilibrium concentration in solution (mg L^{-1}), K ($mg^{1-1/n}L^{1/n}kg^{-1}$) is the Freundlich adsorption coefficient and 1/n is a describer of isotherm curvature. The values of 1/n during adsorption of three carbamate pesticides on six different soils were less than unity (0.830- 0.950) indicating a convex or 'L' type of isotherm (Figs. 1-3) (Giles *et al.,* 1960; 1974). These kinds of isotherm arise because of minimum competition of solvent for sites on the adsorbing surface. The slope of the isotherm steadily decreases with the rise in solute concentration because vacant sites become less accessible with the progressive covering of the surface. The curvilinear isotherm suggests that the number of available sites for the adsorption become a limiting factor. The adsorption was in the order pesticide III > I > II, which is supported by the values of K (31.6- 56; 30.2- 53.5 and 32.6- 60.2 for pesticides I, II, III respectively) and 1/n (0.835-0.935; 0.830- 0.900 and 0.855- 0.950 for pesticides I, II, III respectively). The adsorption of all the three carbamate pesticides follows the order soil 1 > 2 > 3 > 4 > 5 > 6.

The carbamate pesticides adsorption isotherms for organic material amended soils are given in Fig. 1. The isotherms were non-linear. The adsorption of pesticides in organic manure amended soil was more than in unamended soils. This increase could be related to the sorption of organic matter to the soil by increasing the sorption sites available for adsorption. The interaction between pesticide and organic manure occur via multiple bonding mechanisms including ionic bond between negative charged organic matter and positively charged pesticides and/or hydrogen bonds in between pesticides and organic matter as (Villavarde *et al.,* 2008).

The adsorption of pesticides in presence of organic manure followed the order sewage sludge > FYM > poultry manure which may be correlated with organic carbon content. The values of Kd (distribution coefficient) [Kd = (X/m) /Ce] were 42.5-8.4; 40-7.3 and 31.7-6.7 for sewage sluge, FYM and poultry manure amended soils respectively, confirming the above inferences. The values of Kd increases with the addition of organic manure (28-8.2 to 42.5-13 on amending 0-5 g sewage sludge kg^{-1} soil). The values were minimum in unamended soil No. 6 and maximum in sewage sludge amended soil 1. These results confirm the role of organic matter as the primary adsorbing component for the studied pesticides.

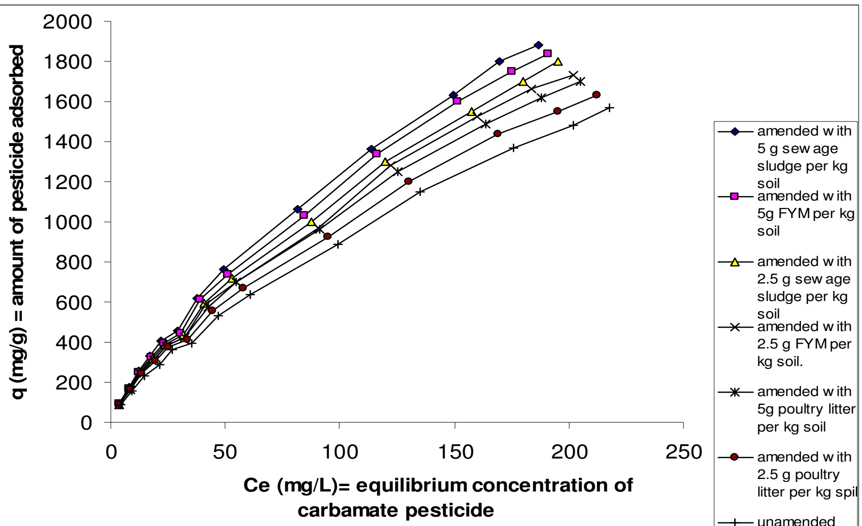

Fig 2 Effect of organic manure on the adsorption of pesticide II on soil 1.

Desorption results indicate that part of the pesticide adsorbed can be desorbed by water. The desorption isotherms followed the same pattern as that of adsorption. Desorption was in the order pesticide II > I > III. The desorption in unamended soil was more than in amended soil and followed the order unamended > poultry manure > FYM > sewage sludge, denoting that organic manure adversely affects desorption due to less availability and more retention of pesticide by organic carbon. The desorption isotherm also obey Freundlich equation. With increasing level of organic manure (0-5 g kg^{-1} soil) the value of Freundlich desorption coefficient K' increased (49.9 to 59.4 for sewage sludge amended soil 1)and 1/n' decreased (0.880 to 0.865 for sewage sludge amended soil 1) , the higher values of K' was indicative of difficult desorption.

The values of Freundlich adsorption coefficient (K) was significantly positively correlated with soil organic matter (r = 0.806-0.845) and negatively correlated with soil pH (r = 0.694 - 0.694) for all the three studied pesticides on all the six studied soils. These data also support our mechanism of adsorption.

From these studies it may be concluded that carbamate pesticides adsorbed by organic material amended soil may be retained for a longer time in the soil and control the pesticidal activity effectively. These results also suggest the possibility of using organic material to develop physico-chemical methods for preventing the pollution of soils and waters by pesticides and for eliminating pesticide residues from this media.

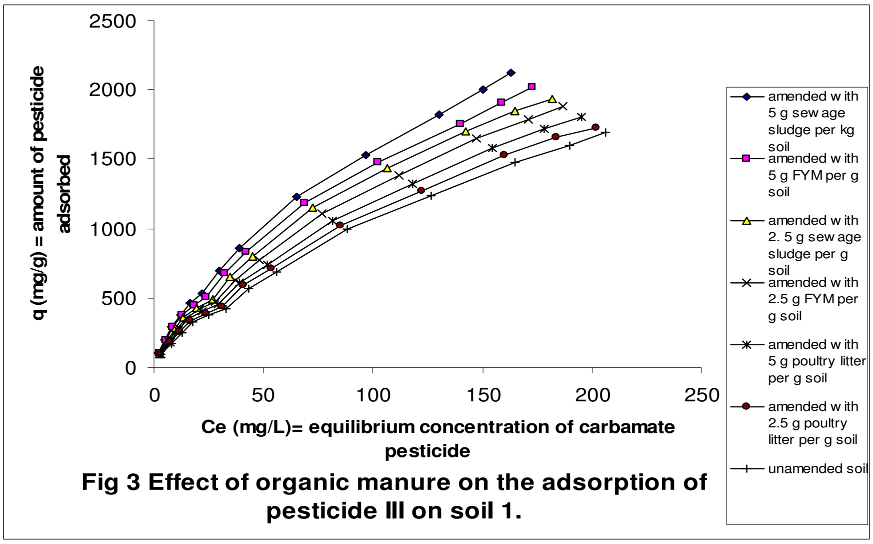

Fig 3 Effect of organic manure on the adsorption of pesticide III on soil 1.

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