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Influence of Soil Properties on the Adsorption of Carbofuran in Soil.

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In an Experiment for Studying the influence of soil it was found that adsorption of carbofuran was highest in laterite soil and decreased sequentially in black alluvial and red soils. Soil organic matter was a more potent adsorber of carbofuran than the minernal fraction. The Multiple linear regression analysis showed that soil organic matter alone contributed 98 per cent of the total adsorption of carbofuran in soils.

Once a pesticide finds its way into the environment, a major part of it comes in contact with soil. In the soil, the biocides are either totally deactivated or thier biocidal efficacy gets reduced in several ways such as adsorption, leaching, volatilization, decomposition, etc. Adsorption influences almost all the reactions of pesticides in soil. Firstly, as a result of this process, the added toxicant loses its bio-activity; secondly, adsorption restricts the movement and hence prevents the chemical from reaching the target and finally the adsorbed compound persists in soil for a longer time, thus creating problems of pollution. This phenomenon, therefore, appears to be one of the major factors affecting pestieide soil interactions. Carbofuran being a soil applied insecticide, its availability for plant uptake, movement in soils, chemical persistence and biological efficacy are mainly dependent on adsorption - desorption processes of the soil. This paper contributes to the study of the influence of properties on the adsorption of carbofuran in soil.

MATERIAL AND METHODS

Four surface soils, representing the major soil, groups of Tamil Nadu (India) viz., red, black, alluvial and laterite were selected for the study. The natural soils, their clay fractions and the organic matter oxidised soils were used as adsorbents. The organic matter in soils was removed by H_2O_2 oxidation. In red, black and alluvial soils, the organic matter was completely oxidised while in laterite soil only partial oxidation was carried out. The organic carbon content before and after oxidation was determined by Walkley and Black wet combustion method. The difference in the quantities of carbofuran adsorbed on the original soil sample and that on H_2O_2-treated sample was considered as due to the effect of organic matter. The natural as well as the organic matter, oxidised soils were ground to pass through 0.5mm sieve for the adsorption studies. The clay fraction was also isolated.

Aqueous solution of carbofuran was prepared by adding carbofuran (99.9%) to distilled water and mixed well by a magnetic stirrer for 24 to 48 hr. and the concentration in the final solution was determined and adjusted to a convenient concentration.

Aliquotes of 1 g of soil (natural and organic matter oxidised) of 0.5 g clay samples of each soil were transferred to a series of stoppered centrifuge tubes and were added different aliquots of stock solution so as to give a convenient range of 20. 40, 60, 80, and 100 g of carbofuran/g of adsorbent and the final volume of the suspension was made up to 25 ml with distilled water. The tubes were then stopperd tightly and shaken for 6 hr. in an end over end shaker and centrifuged for 15 min. at 2500 rpm. The concentration of carbofuran in a suitable aliquot of the supernatent solution was estimated by the method of Gupta and Dewan (1971)

The quantity of carbofuran adsorbed was calculated from the difference between the amounts initially added and the quantity remaining in the equilibrium solution. The data were plotted as per Freundlich adsorption equation, since this could be applied to such heterogenous system like soil-pesticide-water supension as :

$X/m = KC^{1/n}$ where

X/m = Quantity of carbofuran adsorbed per unit weight of the soil or clay (g/g).

C — equilibrium concentration (ppm)

'K' and 'n' are constants

The constants 'k' and 'n' were obtained respectively from the intercept and reciprocal of the slope of straight line graph obtained upon plotting the data on a log-log scale ie.

$$\log X/m — \log K' + 1/n \log C.$$

The adsorption capacity of organic matter and the contribution made by the clay and organic matter were calculated from the basic adsorption values in the natural and organic matter oxidised soils. The relationship of 'kd' values with organic matter, clay, CEC, pH, EC and total sesquioxides was worked out by simple correlation and multiple linear regression analyses for the correlation studies the data generated from 16 soils (4 each in red, black, alluvial and laterite) were utilised.

RESULTS AND DISCUSSION

The data on the adsorption of carbofuran on natural organic matter oxidised soils and their clay fractions are presented in the form of adsorption isotherm. Freundlich equation was used for fitting the isotherms in the present study. Although the Freundlich equation is empirical, this equation is best suited for such heterogenous system like soil-pesticide-water system. While Freundlich's constant 'k' denotes the quantity of the adsorbate adsobed when its concentration in the equilibrium solution is at unity, the value of constant 'n' serves as a measure of the energy of adsorption (Balley and White 1970). In the present study, the Freundlich equation has been employed mainly to find out the adsorbability based on the values of 'k'.

According to the system of classification of adsorption isotherm given by Giles *et al.* (1960), the isotherm obtained in the present study in all the 4 soils were of L-type. This indicated that the soils as well as their clay fractions possessed a high affinity for adsorption of carbofuran.

The Freundlich's adsorption constants for the adsorption of carbofuran on soils and clays are given in Table 1. The 'k' values for red, black alluvial and laterite soils were 9 09, 15.14, 9. 56 and 70.79 respectively. The adsorption of carbofuran on organic matter oxidised soils was lower than natural soils. On a unit weight basis, the clays adsorbed larger quantity of the compound than the natural or organic matter oxidised soils except in laterite soil where the clays adsorbed less amount of carbofuran than the other two adsorbent. The distribution coefficient 'kd' (ratio of the quantity of a compound adsorbed per unit weight of the adsorbent to the equilibrium concentration) another useful parameter was also determined. The 'kd' value was highest in laterite soil, followed sequentially by black, alluvial and red soils

Variations in the contents of organic matter and clay, and pH of the various types of soils were partly responsible for the observed differences. Laterite soil with low pH and containing 3.63 per cent of organic matter, adsorbed highest amount of carbofuran. Although clay content and surface area of black and alluvial soils were higher than those of laterite soil. the extent of carbofuran adsorption did not vary with these properties. The contents o clay and organic matter were low in red and alluvial soils and hence least adsorption of carbofuran was observed in these soils. Jamet and Piedallu (1975) also observed that the adsorption o carbofuran in 9 types of soils increased with increase in organic matter conten and the isotherms of carbofuran adsorption and desorption satisfied the Freundlich equation

The contents of organic matter ir soils before and after oxidation wer determined. In red, black and alluvial soils the organic matter was completely oxidised and in laterite soil the organic matter content was reduced to 0.59 per cent from 3.63 per cent by partial oxidation.

There was a considerable reduction in the adsorption of carbofuran on organic matter oxidised soils when compared to the natural soils. The reduction was highly pronounced in laterite soils where in the organic matter content was higher than the other type of soils. The decrease in adsorption capacity of soils following oxidation or organic matter suggested that the organic matter fraction might have contributed much towards the adsorption. Therefore, the adsorption capacityof organic matter and the contribution made by the clay and organic matter were calculated from the basic adsorption values in the natural and organic matter oxidised soils. The difference in adesorption between natural and oxidised soil at several concentration of the equilibrium solution were calculated according to the procedure given by Saltzman et al. (1972). The adsorption per unit weight of organic matter was calculated as the ratio between each of these values and the amount of organic marter lost by oxidation. From the calculated adsorption curves. a quantitative evalution of the adsorptive capacity of organic surface was also made. The adsorption capacity of the organic matter expressed as distribution coefficient (kd) was 363.36, 705.12, 361.44 and 1322.00 for red, black, alluvial and laterite soils respectively. But the 'kd' values for clays separated from the soils were 5.00, 9.50, 5.50 and 20.00 for red, black, alluvial and laterite soils respectively. This clearly explained why the adsorption of carbofuran was higher in laterite soil than the other type of soils.

Further the relationship of 'kd' values with organic matter, clay, cation exchange capacity, pH, soluble salts (Ec) and total sesquioxides was worked out by simple correlation and multiple linear regression analyses. In simple correlation studies, organic matter of soils was found to be highly correlated with 'kd' values (r = 0 980) while pH and Ec were found to be negatively related. None of the other variables had significant relationship with 'kd' values. Multiple linear regression analysis showed that only organic matter and pH were significantly related with 'kd' values of carbofuran adsorption. The former was positively related while the latter was negatively correlated. The affinity or organic matter towards the carbofuran was so great that the organic matter of soils contributed over 98 per cent of the total adsorption.

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TABLE 1 Certain physical and Chemical Characteristics of the soils used for the study.

Property/Constituent.	Red	Black	Alluvial	Laterite
Clay %	16 95	40.90	20.87	25.25
Textural class	Sandy loam	Sandy clay	Sandy clay loam	Sandy clay loam
pH.	7.9	8.2	7.8	5.2
Organic matter %	0.55	0.76	0.80	3.63
Organic matter in H_2O_2-Oxidised soil	—	—	—	0.59
Total sesquioxide	10.10	12 97	9.72	10.66

TABLE 2

Adsorption of carbofuran by soil and their clay fractions.

Soil type	Adsorbent used	Freunclich 'K'	Freunclich 'n'	(kd'values (Mg/g)	Contribution of soil organic - matter and mineral fraction (kd values towards adsorption). Organic matter	Mineral fraction
Red	NS	0.09	0.89	6.00	3 50 (636.36)	5.00
	OS	4.52	0.67	4.50		
	CL	18.41	1.05	16.50		
Black	NS	15.14	0.95	15.00	5.50 (705.12)	9.50
	OS	7.41	0.80	6.50		
	CL	32.14	1.02	35.00		
ALLUVIAL	NS	9.56	1.08	10.00	3.00 (361.44)	55.0
	OS	5 31	0.79	6.00		
	CL	18.51	1.16	19.00		
Laterite	NS	70.79	0.69	72.00	48.00 (1322.00)	20.00
	OS	32.59	0.77	32.00		
	CL	18.62	0 92	25.00		

Figures in parantheses in indicate the adsorption capacity of soil organic matter per unit weight (calculared values)

NS : Natural soil
OS : Organic matter oxidised soil
CL : Clay