Bull. Environ. Contam. Toxicol. (1997) 59:65-71
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Bulletin of Environmental Contamination and Toxicology

Sorption of Carbaryl(1-Napthyl N-Methyl Carbamate) by Soil

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Received: 21 September 1996/Accepted: 21 February I997

Carbaryl (1-napthyl N-methyl carbamate),a contact insecticide with slight systemic properties, is widely recommended for use in agriculture against many insect pests of cereals , fruits, vegetables, and other crops. Applied carbaryl to soil either directly or indirectly, comes into contact with a variety of surfaces upon which adsorption can occur. The adsorption-desorption of pesticide by active soil surfaces is one of the main processes controlling soil pesticide interaction (Saltzman et al. 1972) and the sorption phenomena can influence the translocation, volatility, persistence and bioactivity of a pesticide in soil(Bailey and White 1970). With that end in view the present approach aims at the investigation of sorption pattern and mechanisms of adsorption of carbaryl on some soil of West Bengal, India.

MATERIALS AND METHODS

Four surface soils (0-20 cm) were collected from different cultivated soil areas of West Bengal with no recent history of pesticide application. Among them, two were lateritic soils of Bolpur (Soil No 1.) and Nalhati (Soil No.11) in the district of Birbhum while the other two were Terai alluvial soils of Barokodali (Soil No. III) and Dudherkuthi (Soil No. IV) situated in the district of Coochbehar. The soil samples were air dried, crushed and sieved through a 80-mesh sieve. The relevant physico-chemical characteristics of the soils are given in table 1.

A pure sample of carbaryl was obtained by the recrystallization of a technical grade sample supplied by M/s. Rhone-Poulenc Agrochemicals (I) Ltd.

To established the insecticide adsorption equilibrium in relation to time on the soil systems, 20 mL of insecticide solution (in 0.02M $CaCl_2$) was added to 2 g of air-dried soils in 50 mL glass centrifuge tubes, Triplicate samples plus blanks (without soil) were shaken for 0.25, 0.5,1 ,2, 2.5, 3, 6, 12, 24 and 36 hr. The tubes were centritiged for 30 min at 2000 rpm. Suitable aliquots were then taken from the collected centrifugate for estimation of the insecticide.

To determine the sorption pattern, the method was essentially the same as

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Table 1. Some physico-chemical characteristics of the experimental soil.

Characteristics	Bolpur (I) (Ultisol)	Nalhati (II) (Ultisol)	Barokodali(III) (Inceptisol)	Dudherkuthi(IV) (Inceptisol)
Organic Carbon(%)	0.234	0.675	0.990	0.640
Organic Matter(%)	0.40	1.16	1.70	1.10
pH(1:2.5 ratio)	5.0	6.1	5.4	5.9
EC(dSm^{-1})	0.34	0.61	0.15	0.16
CEC(C mol P^+Kg^{-1})	6.4	14.5	13.9	12.6
Clay content(%)	19.15	31.60	25.35	23.75
Free Fe_2O_3(%)	1.32	1.70	1.23	0.87
Free Al_2O_3 (%)	0.42	0.73	0.77	0.67
Surface Area (m^2g^{-1})	75	97	112	103

adopted by Felsot and Dahm (1979) with some modifications. Stock solution of carbaryl was made in 0.02 M CaC1_2 at concentration below their water solubility. The stock was diluted with 0.02 M CaC1_2 solution to obtained seven different concentrations that were used for the experiment. Two grams of air dried soils were shaken with 20 mL solution of carbaryl (0.4-24.0 ppm) in 50 mL glass centrifuge tubes for 3 hr at the room temperature(30 ±l°C). All treatments were performed in triplicate, and appropriate blanks (without soil) at each concentration were run side by side. The tube containing the eqilibriated materials were centrifuged at 2000 rpm for 30 min and the centrimgates were decanted from which 5 mL aliquots were taken for analysis of the insecticide by visible absorption spectrophotometry. The amount of carbaryl adsorbed (μg g^{-1} soil) was obtained simply by subtracting the value obtained from the blank and the treatment by using the relation:$A = V/m (C_B - C_e)$ Where, A = amount adsorbed, V = solution volume, m = grams of soil taken, C_B = equilibrium concentration of blank and C_e = equilibrium concentration of treatment supematant (Green and Yamane 1970).

After centrifugation and removal of the supematant , 20 mL of 0.02 M CaC 1_2 solution were added back to the tubes and the samples were shaken for further 3 hr. The tubes were centrifuged and 5 mL of supematant solution from each tube were removed for the spectrophotometric determination of the desorbed carbaryl. Desorption, expressed as micrograms adsorbed / gram of soil (ug g' soil), was obtained from the difference, taken into account the solution remaining in the soil after the supernatant was poured off,

The spectrophotometric determination of carbaryl was done by following the method of Stansbury and Miskus (1964) with some modifications. 5 mL of 0.5 N NaOH were added to 5 mL aliquot from the centrifugate taken in a 25 mL volumetric flask followed by 5 mL of 0.03% (wt/vol) methanolic solution of p-nitrobenzene diazonium fluoborate. The mixture was then diluted to 25 mL with methanol and after 30 min absorbance of the greenish-blue colour of the solution was measured at 590 nm using a spectrophotometer (Bausch-Lomb Spectronic 20).

RESULTS AND DISCUSSION

The adsorption equilibria for carbaryl studied on the soils of Bolpur (Soil No.I) and Barokodali (Soil No.III) show (Figure 1) that the adsorption gradually increased with the passage of shaking time and reached a maximum after 3.0 hr for Bolpur soil and 2.5 hr for Barokodali soil The absence of rapid initial increase of adsorption indicated that interaction between carbaryl and soil samples was of a kind other than ion exchange(Bunzl et al. 1976) and the equilibrium seemed to be fully attained within 3 hr.

In order to know the behaviour of adsorption with increasing concentration of carbaryl, the amounts of the insecticide adsorbed were plotted (Figure2) against the equilibrium concentrations of the insecticide for each soil. The adsorption isotherms thus obtained yielded S- shaped curves as described by Giles et al. (1960) which suggest multilayer adsorption and vertical orientation of adsorbed pesticide molecules at the adsorbent surface with the availability of new sites to the solvent as adsorption occurs. It also indicates that solvent and solute compete each other for adsorption sites on the soil colloidal surface. The upward nature of the curves show that after complete adsorption on adsorbent surface, adsorbate molecules attract each other and get associated to a considerable extent (Adhikari et al. 1991).

Adsorption-desorption of carbaryl has been successfully described with the Freundlich model. Mass dimension (microgram/gram) values were fitted by linear regression to the log form of empirical Freundlich adsorption equation: log x/m = log K + l/n log C_e When ,x = µg of carbaryl adsorbed , m = wt of soil (g), C_e= equilibrium concentration of the adsorbate in solution (µg/mL) and K and, l/n are two constants .The constant K has been variously defined as the adsorbent capacity for the adsorbate (Adamson 1967) and the extent or degree of adsorption (Hamaker and Thompson 1972) The K values can be used to compare sorption of different pesticides on various soils at unit concentration (i.e, Ce=lµg/mL) , where K=x/m. The significance of l/n is more obscure than that of K and it provides a rough estimations of the intensity of adsorption (Adamson 1967).

The log-log plots of carbaryl sorption (log x/m vs log C_e) yielded straight lines from which the value of K and l/n (Table 2) for carbaryl on each soil were obtained as the intercept and slope, respectively. All regression lines generated had a coefficient of determination of at least 0.98, which indicates an excellent fit of the data by Freundlich equation.

As illustrated by the values of constants Kandl1/n,the decreasing sequence of the adsorption capacity of soils for carbaryl are Barokodali > Nalhati>Dudherkuthi> Bolpur which followed the same order as the order of organic matter content of the soils (Table 1).The results find support from some earlier studies (Khan et al. 1987, Singh et al 1990, Adhikari et al. 1991) which have shown that organic matter content of soils significantly influence the adsorption of pesticides The intensity of carbaryl adsorption as indicated by the values of l/n are greater than unity for all

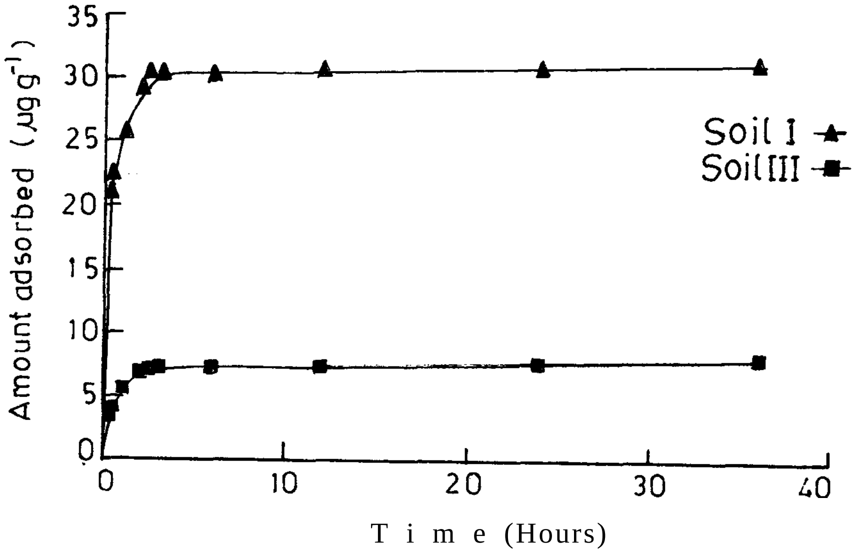

Figure 1 The effect of time on adsorption of carbaryl by Bolpur (I) and Barokodali(III) soil.

the soils and follow the order:Dudherkuthi>Barokodali>Bolpur>Nalhati.The variable slopes of the sorption isotherms obtained for the different pesticide-soil systems studied reveal that pesticide sorption on soil is a complex phenomenon involving different types of adsorption sites with different surface energies (Felsot and Dahm 1979).

Desorption isotherms represent the microgram of insecticide still adsorbed per gram of soil as a function of equilibrium concentration after one desorption cycle. Adsorption was reversible, but the desorption K values were consistently higher than those for adsorption (Table 2). This is because of higher amount of carbaryl retained after desorption than that for adsorption at unit equilibrium concentration. Hysteresis phenomena from the desorption isotherms indicate that the different range or spectrum of forces are involved in adsorption of the carbaryl on the soils than in desorption (Wahid and Sethunathan 1978, Graham and Conn 1992).

Table 2. Values of Freundlich parameters for the sorption of carbaryl on soils at 30°C.

Soil	Adsorption		Desorption	
	K	l/n	K	l/n
Bolpur	0.308	1.554	1.216	1.428
Nalhati	2.175	1.385	6.429	1.409
Barokodali	2.490	1.747	10.016	1.624
Dudherkuthi	1.916	2.099	3.792	2.491

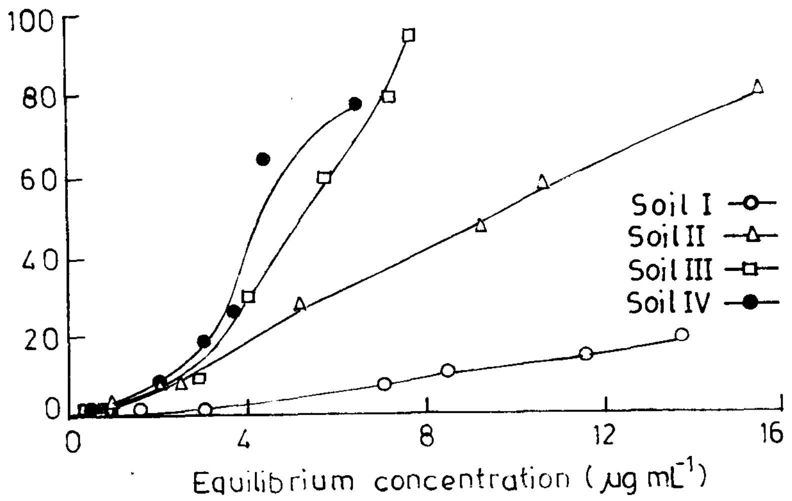

Figure 2. Adsorption isotherms of carbaryl on soil.

The relationship between sorption and soil properties was determined through simple correlation analysis. Four K values so obtained were correlated separately with the eight physico-chemical characteristics of the soil. In simple correlation analysis, Freundlich K for carbaryl was significantly and positively correlated with organic matter (r=0.952),surface area(r=0.954), CEC(r=0.979) and free Al_2O_3 (r=0.998) content of the soils.

Sorption relationship of carbaryl was illustrated in a different manner by normalizing the Freundlich K constants to a 1- g, organic matter basis (Table 3). The new constant, K_{om}(K_{om}= K x 100/ Percent organic matter), was averaged over the four soils. Assuming that the carbaryl was adsorbed mainly by organic matter, the change in free energy for adsorption was calculated for the pesticide by using the mean value for K_{om} and the equation given by Osgerby (1970):ΔG_{om} = -RT In K_{om} Where ΔG_{om} = free energy change (K cal/mol), R= gas constant (2.0 Cal/K mol) and T= Kelvin temperature.

Table 3. Values of thermodynamic parameters associated with sorption of carbaryl on soils.

Soil	Adsorption			Desorption
	K_{om}	K_0	ΔG^0 (K cal mol^{-1})	K_{om}
Bolpur	77.00	2.88	-0.641	304.00
Nalhati	187.50	4.42	-0.900	554.22
Barokodali	146.88	4.50	-0.911	589.17
Dudherkuthi	174.18	4.18	-0.866	344.72
Average K_{0m}	146.39			448.02
ΔG_{om}	-3.021			-3.699

The ΔG_{om} was negative (calculated for 303°K) and illustrated that adsorption of carbaryl on soil was a spontaneous process (Table 3). However, low values of ΔG_{om} reveal more or less physical nature of the adsorption on the soil organic matter surface. The values of thermodynamic equilibrium constant, K_0 (or the thermodynamic distribution coefficient) and standard free energy, ΔG^0, of adsorption for carbaryl on each soil were calculated by the method of Biggar and Cheung (1973). Values of K_0 were obtained by plotting In (C_s/C_e) vs C_s and extraploating to zero C_s.Here, C_s is µg of solute adsorbed per mL of the solvent in contact with the adsorbent surface and C_e is µg of solute per mL of the solvent in the equilibrium solutions; C_s was calculated according to the following equation: $C_s = (\rho/M)A/\ S/N(x/m)$ Where ρ = density of solvent (g/mL), M= molecular weight of the solvent (g/mole), A= cross-sectional area of the solvent molecule (cm^2/molecule,) N = Avogadro's number (6.023×10^{23} molecules/mole), S = surface area of the adsorbent (cm^2/g) and x/m = specific adsorption (µg/g).The cross-sectional areas of the solvent molecules were estimated from the following equation: $A = 1.091 \times 10^{-16}[(M \times 10^{24}) / (Np)]^{2/3}$ Where, A=cross-sectional area of the solvent molecule (cm^2/mole), N=Avogadro's number (6.023×10^{23} molecules/mole) and M and r are respectively, the molecular weight (g/mole) and the density (g/mL) of the solvent.

Thus, by obtaining K_0, the standard free energy, ΔG^0 for the adsorption was calculated from the equation: $\Delta G^0 = -RT \text{ In } K_0$. The negative values of ΔG^0 (Table 3) in all cases indicated the spontaneous nature of adsorption of carbaryl on the soils. Low values of ΔG^0 further reveal that adsorption of carbaryl is more or less physical in nature.

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