

Sorption of oxadiargyl and butachlor in selected soils of Andhra Pradesh

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ABSTRACT

Adsorption-desorption was studied by batch equilibrium technique at $37\pm 1^\circ\text{C}$ at different concentrations of oxadiargyl and butachlor in selected soils of Andhra Pradesh. Desorption isotherms showed a considerable hysteresis which was more prominent when desorption was carried out at higher concentrations of adsorbed oxadiargyl and butachlor. Desorption isotherms at lowest level of adsorbed herbicide concentration were close to adsorption isotherms. The cumulative desorption after five desorption steps was significantly different for all the initial concentrations of adsorbed herbicide for all the soils. Desorption of these herbicides was higher in Alfisol than Vertisol, might be attributed to low organic carbon and low clay content. The variation in per cent desorbed may be due to heterogeneity involved in different soils, that vary widely in type and energy of bonding. Desorption isotherms confirmed to Freundlich's equation and the Freundlich's constants increased with increasing initial concentration of adsorbed herbicide thus confirming the irreversible nature of the adsorption of oxadiargyl and butachlor on these soils.

Key words: Oxadiargyl, Butachlor, Adsorption-desorption, Andhra Pradesh.

Use of herbicides for the control of weeds has become imperative especially in the irrigated agriculture for a wide variety of reasons like non availability of labour, high labour cost, unfavorable climatic conditions for weeding *etc.* As a result, herbicide usage in Andhra Pradesh, increased 34.35 times from 2006 to 2009 (Annual report 2009). When a herbicide is applied to soil, it undergoes a number of processes which determines its fate in soil. Adsorption-desorption is an important process for determining the ultimate fate of herbicides in soil because detoxification mechanisms such as degradation, metabolism, microbial uptake and mobilization are operative only on the non-sorbed fractions of the chemical to the sites on soil mineral or organic surfaces. Adsorption decreases the concentration of chemical leading to its decrease in adsorption-desorption influences mobility, persistence, degradation and volatility of pesticide in soil (Kalpana *et al.* 2002). Adsorption and desorption are involved in determining the ease by which herbicides move through the soil profile and also their plant availability and microbial degradability, thus persistence. This study was carried out for adsorption-desorption of oxadiargyl and butachlor in four soil types of Andhra Pradesh.

MATERIALS AND METHODS

Experiments were conducted at All India Coordinated Research Programme on Weed Control, Acharya N G Ranga Agricultural University, Hyderabad, with two

Alfisols (A4: ARS, Anantarajpeta and A8: Karimnagar) and two Vertisols (V2: RARS, Lam and V3: Kurnool) of Andhra Pradesh during 2007-2008. Representative soil samples were collected from the surface horizon with no background of oxadiargyl and butachlor application. The soils were air dried and passed through a 2 mm sieve. The physico-chemical properties of these soils were analysed by using standard procedures.

Technical grade oxadiargyl (98% purity) and butachlor (86.87% purity) were obtained from M/S Bayer Crop Science, Mumbai and from M/s Hyderabad Chemicals, Hyderabad, respectively. Adsorption studies were conducted using the batch equilibration technique.

Adsorption-desorption studies were conducted by equilibrating 5g of soils (<2 mm) with given initial concentrations of oxadiargyl *viz.*, 0, 5, 10, 15, 20, 25, 30 and 35 $\mu\text{g/ml}$ and butachlor 0, 20, 40, 60 and 80 $\mu\text{g/ml}$ in 1×10^2 M CaCl_2 solution. The final volume of equilibrating solution was made up to 20 ml with distilled water and incubated for 24 hrs at $37\pm 1^\circ\text{C}$. After incubating, the soil suspension was centrifuged. Five ml of supernatant was taken out and absorbance of oxadiargyl and butachlor was measured at 226 nm and 410 nm, respectively. To the remaining slurry containing 15 ml solutions of oxadiargyl or butachlor and soil, 5 ml of CaCl_2 solution (1×10^2 M) was added, again incubated for 24 hrs and centrifuged to determine the equilibrium concentration. This process was

repeated for 5 consecutive days. Identical soil blanks were also maintained simultaneously and the net absorbance of equilibrium concentration at each stage was obtained by subtracting the absorbance of blanks. The desorption experiment was carried out in quadruplicates. The amount of herbicide desorbed was calculated as follows :

$$C_o^n = C_e^{n-1} \times 15/20$$

Where,

C_o^n = initial concentration of herbicide on n^{th} day

C_e^{n-1} = equilibrium concentration on $(n-1)^{th}$ day

Amount desorbed on n^{th} day is given by $(C_e^n - C_o^n) \times 20$. For example. The amount of oxadiargyl desorbed on the 5^{th} day is calculated as $(C_e^5 - C_o^4 \times 0.75) \times 20$. The data was subjected to mathematical analysis by Freundlich equation.

Desorption was carried out on selected Vertisols and Alfisols of Andhra Pradesh over a period of 5 days by successive withdrawal and dilution of supernatant and re-establishment of equilibrium of soils on which the herbicide was previously absorbed. The most commonly used method to characterize adsorption desorption has been batch equilibrium technique (Bist *et al.* 2005, Pandey and Agnihotri 2000, Rai *et al.* 2000, Shanti *et al.* 1997,

Clay and Koskinen 1990, Kosiknen and Cheng 1979).

RESULTS AND DISCUSSION

Desorption of oxadiargyl and butachlor from selected Vertisols and Alfisols

The adsorption of these herbicides increased with their initial concentration of herbicide and this phenomenon was quite common in adsorption studies (Shanthi *et al.* 1997, Prakash and Suseela Devi 1998, Rai *et al.* 2000, Nagamadhuri 2003). The isotherms indicated that greater amount of herbicides were adsorbed in soils ($V_2 > A_8 > V_3 > A_4$). The higher adsorption on V_2 may be due to high organic carbon content. Similar observations were made for greater surface adsorption of butachlor in soils having high organic matter content. Similar observations were made by Rai *et al.* (2000) and Singh (1996) for greater surface adsorption of pendimethalin in soils having high organic matter content.

At low level of initial concentrations of the adsorbed herbicides, the desorption isotherms were close to adsorption isotherms there by indicating an increase in the degree of irreversibility in adsorption desorption. The cumulative per cent of oxadiargyl and butachlor desorbed at the end of desorption stages is presented (Tables 4 - 6 and Fig. 1 to 4). Desorption of these herbicides was higher in Alfisols (Fig. 2 and 4) than vertisols (Fig. 1 and 3).

Table 1. Physico-chemical and textural characteristics of four selected soils of Andhra Pradesh

Soils	pH	EC (dS/m)	OC (g/kg)	Texture (%)		
VERTISOLS						
V ₂ - RARS, Lam	7.82	0.22	0.85	Sand	Silt	Clay
V ₃ - Kurnool	8.65	0.29	0.45	55.8	11.0	33.20
ALFISOLS						
A ₄ - ARS, Ananthapur	7.71	0.24	0.67	84.4	2.00	13.60
A ₈ - Karimnagar	6.57	0.16	1.06	74.4	3.00	12.60
				76.0	0.4	23.60

EC- Electrical conductivity, OC- Organic carbon

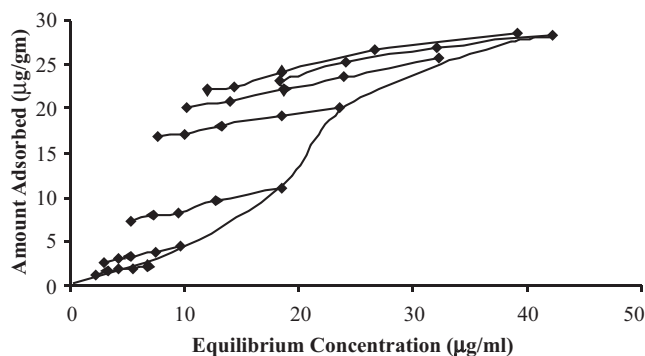


Fig. 1. Sorption isotherms of oxadiargyl in Vertisol -2

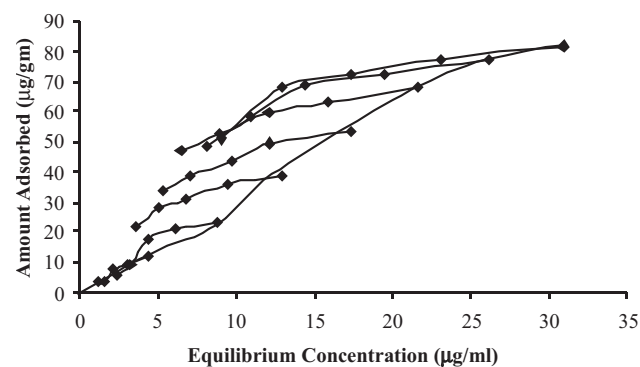


Fig. 2. Sorption isotherms of oxadiargyl in Alfisol -4

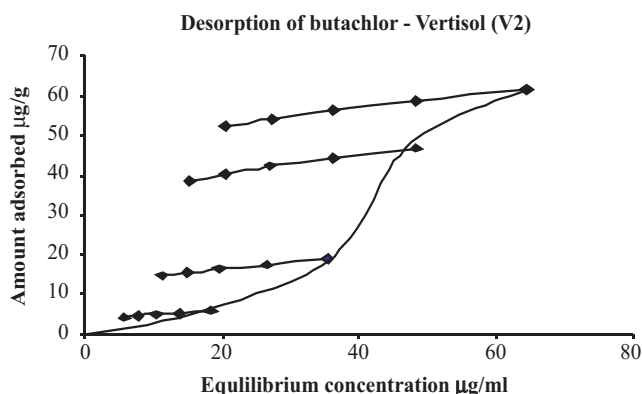


Fig. 3. Sorption isotherms of butachlor in Vertisol - 2

Higher desorption in this soil may be attributed to low organic carbon and low clay content. The variation in per cent desorbed may be due to heterogeneity involved in different soils, that vary widely in type and energy of bonding. In general, higher amounts of herbicide was desorbed during first washing and the amount progressively decreased with each subsequent washings. The per cent cumulative desorption revealed that the adsorption of these herbicides is almost irreversible indicating that the soil organic matter and clay content plays an important role in the adsorption-desorption of oxadiargyl and butachlor from soil solution affecting the bio availability of herbicides in soil. As observed from the adsorption-desorption data of oxadiargyl and butachlor, the desorption peaks exhibited pronounced hysteresis in all the soils and for every level of initially adsorbed herbicide (Fig 1 to 4). The desorption was more pronounced when it was carried out at higher levels of

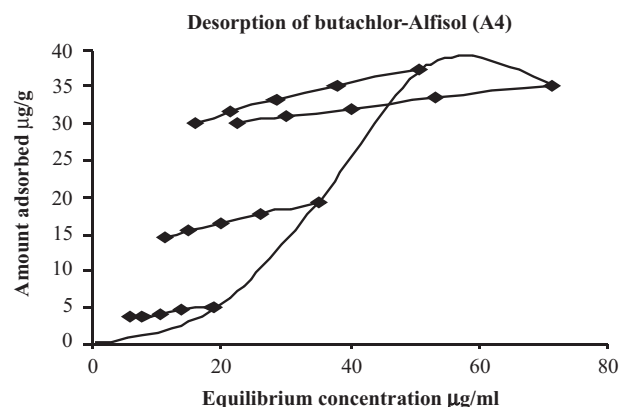


Fig. 4. Sorption isotherms of butachlor in Alfisol 4

adsorbed herbicide. At lower levels adsorption isotherms were very close to desorption isotherms, thus indicating irreversibility of adsorption-desorption mostly with increase in sorbed herbicide. The per cent cumulative desorption in all the soils decreased with an increase in the amount initially adsorbed herbicide.

The Freundlich constants K_F values for desorption isotherms were found to be increased with increasing initial concentrations of the herbicides. Larger K_F values for adsorption than for desorption indicate stronger binding of herbicides to the soils (Table 2 and 3). The cumulative percentage of the herbicides adsorbed at the end of the desorption stages indicate that the per cent desorbed in all the soils and for the herbicides used in the study decreased with increase in the amount initially adsorbed. The significant variations in the cumulative desorption between all soils and at different levels of

Table 2. Freundlich constants (K_F and n) for desorption of oxadiargyl from selected Vertisols and Alfisols

Soil No.	Initial concentration(µg/ml)								% Cumulative desorbed
	20		40		60		80		
	K_F	n	K_F	n	K_F	n	K_F	n	
V ₂ - RARA, Lam	0.62	0.625	0.4	0.55	0.82	0.75	0.3	0.9	42.48
V ₃ - Kurnool	0.28	0.45	0.36	0.44	1.12	0.3	0.66	0.5	36.25
A ₄ - ARS, Ananthapur	0.22	0.4	0.42	0.88	0.38	1.01	0.18	0.66	43.58
A ₈ - Karimnagar	0.58	0.3	0.74	0.50	0.52	0.37	1.12	0.75	52.54

Table 3. Freundlich constants (K_F and n) for desorption of butachlor for selected Vertisols and Alfisols

Soil No.	Initial concentration(µg/ml)								% Cumulative desorbed
	20		40		60		80		
	K_F	n	K_F	n	K_F	n	K_F	n	
V ₂ - RARS, Lam	0.62	0.62	0.40	0.55	0.82	0.75	0.30	0.90	38.56
V ₃ - Kurnool	0.28	0.45	0.36	0.44	1.12	0.30	0.66	0.50	42.84
A ₄ - ARS, Ananthapur	0.22	0.40	0.42	0.88	0.38	1.01	0.18	0.66	45.32
A ₈ - Karimnagar	0.58	0.30	0.74	0.50	0.52	0.37	1.12	0.75	48.65

initial concentration of herbicides can be due to the fact that the soil is a heterogeneous entity with sorption sites that vary widely in type and energy of binding. With the increasing amount of adsorbed herbicide, not only the surface sites are occupied but the herbicide may find its way into soil incorporation caused by clay and structural complex polymer net work.

The extent of herbicides was more pronounced as the incubation time increased and that the herbicide recovery decreased with incubation time. The main cause of hysteresis during desorption could be the presence of a number of heterogeneous adsorbing sites of varying energy levels on soils. In addition some modifications could be taking place in the soil itself during adsorption desorption process

Desorption isotherms of oxadiargyl and butachlor relate the amount of herbicide retained on soil matrix to the concentration in soil solution at each desorption step. These desorption isotherms did not coincide with adsorption isotherms. Desorption of both herbicides from soils indicated that slope of desorption isotherms was much lower than the slope of adsorption isotherms and less amount of herbicide was present in equilibrium solution than during adsorption. This effect known as 'hysteresis' was seen in all the soils. Since the adsorption reactions do not always involve any weak, reversible bonding, hysteresis is, therefore, is often observed in adsorption desorption studies in soils. The adsorption of herbicides on to soils and its subsequent desorption is not a single valued relationship and hence a portion of adsorbed herbicide is apparently resistant to desorption. The causes for hysteresis are not well understood. In some cases the hysteresis may be partially due to degradation of compound during equilibration and also by physical and / or chemical properties of soil solution system (Koskinen *et al.* 1979, Koskinen and Cheng 1983) as adsorption desorption data are obtained under changing conditions. Repeated centrifugation of the slurry in batch equilibration was reported to be responsible in some way for hysteresis of some pesticides (Bowman and Sans 1985).

At low level of initial concentrations of the adsorbed herbicides the desorption isotherms were close to adsorption isotherms there by indicating an increase in the degree of irreversibility in adsorption-desorption. The adsorption-desorption isotherms were Freundlich in nature and Freundlich K_f and n values are presented in Table 2 for oxadiargyl and Table 3 for butachlor.

There was a consistent increase in K_f value as the initial concentration increased in all the soils. Which is an indicative of difficult desorption. (Nagamadhuri, 2003; Shanti *et al.* 1997, Gan *et al.* 1996, Ma *et al.* 1993,

Pignatello 1989). The cumulative per cent of oxadiargyl and butachlor desorbed at the end of five desorption stages is presented (Table 2 and 3). Desorption of these herbicides was higher in Alfisol (A_g) (Table 6). Higher desorption in this soil was attributed to low organic carbon and low clay content. Prakash *et al.* (2000) in their studies on adsorption-desorption of butachlor.

Desorption isotherms of soil adsorbed herbicides showed hysteresis, which was more when the desorption was carried out from higher levels of initial concentrations of herbicide solution. At low levels of initial concentrations of herbicide the desorption isotherms were very close to the adsorption isotherms, thereby indicating the degree of irreversibility in adsorption desorption. Hysteresis was more pronounced at higher initial concentrations of herbicides. The cumulative percent of herbicide desorbed at end of time successive desorption stages showed a decrease with increase in the amount initially adsorbed. With increase in initial concentration of herbicide solution from lower to higher concentration, the K_f values increased for all soils.

The variation in per cent desorbed may be due to heterogeneity involved in different soils, that vary widely in type and energy of bonding. In general, higher amounts of herbicide was desorbed during first washing and the amount progressively decreased with each subsequent washings. The per cent cumulative desorption revealed that the adsorption of these herbicides is almost irreversible indicating that the soil organic matter and clay content plays an important role in the adsorption desorption of oxadiargyl and butachlor from soil solution affecting the bio availability of herbicides in soil.

The results obtained on adsorption-desorption of oxadiargyl and butachlor the following inferences could be drawn.

- Desorption isotherms of herbicides for every level of initial concentration of added herbicides in all the soils did not coincide with adsorption isotherms.
- The slope of isotherms for desorption was obtained by desorbing the herbicide adsorbed at the initial concentrations. The slope of desorption isotherms much less than the slope of adsorption isotherms and less amount of herbicide is present in equilibrium solution than during adsorption. Thus, effect is known as “Hysteresis” and was seen in all the soils.
- The degree of irreversibility in adsorption-desorption was much more prominent at low levels of initial concentrations of herbicides as the desorption isotherms were very close to adsorption isotherms.

Table 4. Desorption of oxadiargyl in Vertisol - 3

I.C µg/ml	I Day			II Day			III Day			IV Day			V Day			% C.A
	E.C µg/ml	A.A µg/g	A.D µg/g	E.C µg/ml	A.A µg/g	A.D µg/g	E.C µg/ml	A.A µg/g	A.D µg/g	E.C µg/ml	A.A µg/g	A.D µg/g	E.C µg/ml	A.A µg/g	A.D µg/g	
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	4.14	17.20	3.86	14.32	2.88	3.11	11.42	2.90	2.70	2.42	8.72	2.70	1.31	6.14	2.58	64.30
10	8.52	29.60	7.14	23.54	6.06	6.24	18.64	4.90	5.96	4.16	12.68	5.96	2.69	9.27	3.41	68.68
15	12.66	46.80	9.88	38.12	8.68	7.96	30.11	8.01	7.40	4.98	22.71	7.40	4.01	16.43	6.28	64.89
20	16.54	69.20	12.65	52.64	16.56	10.11	39.18	13.46	10.02	6.88	29.16	10.02	5.24	22.78	6.38	67.08
25	21.02	79.60	17.62	63.71	15.89	11.54	44.22	19.49	7.98	8.19	36.24	7.98	6.65	30.14	6.10	62.14
30	25.51	88.60	21.08	69.84	18.76	18.26	54.18	15.66	12.86	13.18	41.32	12.86	8.07	32.64	8.68	63.16
35	30.58	88.40	26.41	70.66	17.74	22.23	60.14	10.52	9.48	17.24	50.66	9.48	9.68	40.18	10.48	54.55

IC-Initial concentration, EC-Equilibrium concentration, AA-Amount absorbed, AD-Amount desorbed, CD- Cumulative desorption, CA- Cumulative adsorption

Table 5. Desorption of butachlor on Vertisol - 3

I.C µg/ml	I Day			II Day			III Day			IV Day			V Day			% C.A
	E.C µg/ml	A.A µg/g	A.D µg/g	I.C µg/ml	A.A µg/g	A.D µg/g	I.C µg/ml	A.A µg/g	A.D µg/g	I.C µg/ml	A.A µg/g	A.D µg/g	I.C µg/ml	A.A µg/g	A.D µg/g	
20	18.75	5.05	3.78	4.49	0.56	2.84	4.00	0.49	0.38	2.13	3.62	0.38	1.59	3.39	0.23	32.87
40	35.90	16.44	12.33	15.07	1.37	9.24	13.96	1.11	0.88	6.93	13.08	0.88	5.20	12.33	0.75	25.00
60	52.65	29.43	22.07	27.56	1.87	16.55	25.91	1.65	1.46	12.41	24.45	1.46	9.31	23.25	1.20	20.99
80	71.80	32.81	24.60	31.19	1.62	18.45	29.68	1.51	1.36	13.84	28.32	1.36	10.38	27.24	1.08	16.97

IC-Initial concentration, EC-Equilibrium concentration, AA-Amount absorbed, AD-Amount desorbed, CD- Cumulative desorption, CA- Cumulative adsorption

Table 6. Desorption of butachlor in Alfisol - 8

I.C µg/ml	I Day			II Day			III Day			IV Day			V Day			% C.A
	E.C µg/ml	A.A µg/g	A.D µg/g	I.C µg/ml	A.A µg/g	A.D µg/g	I.C µg/ml	A.A µg/g	A.D µg/g	I.C µg/ml	A.A µg/g	A.D µg/g	I.C µg/ml	A.A µg/g	A.D µg/g	
20	18.35	6.60	4.95	5.98	0.62	3.71	5.53	0.45	0.36	2.78	5.17	0.36	2.08	4.89	0.28	25.9
40	33.80	24.80	18.60	23.39	1.41	13.95	22.04	1.35	1.24	10.46	20.80	1.24	7.84	19.84	0.96	20.00
60	47.50	49.20	36.90	46.92	2.28	27.67	44.79	2.13	2.02	20.75	42.77	2.02	15.56	40.84	1.93	16.99
80	56.35	54.60	40.95	52.63	1.97	30.71	50.77	1.86	1.67	23.03	49.10	1.67	17.27	47.51	1.59	12.98

IC-Initial concentration, EC-Equilibrium concentration, AA-Amount absorbed, AD-Amount desorbed, CD- Cumulative desorption, CA- Cumulative adsorption

- The hysteresis was more pronounced when desorption was carried out from higher levels of initial concentration of adsorbed herbicides.
- Desorption of herbicides from both the soils was hysteric. The hysteresis obtained might have resulted from several factors. As the adsorption reactions do not always involve any reversible, weak binding mechanisms hysteresis is often observed during adsorption desorption.

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