



Adsorption of oxadiargyl and butachlor on soil particle size separates

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ABSTRACT

Study on adsorption of oxadiargyl and butachlor was carried out on soil particle size separates of four type of soils from different agroclimatic zones of Andhra Pradesh using batch equilibration technique. Irrespective of the particle size, the per cent adsorption was more in vertisols than alfisols. Among four soils studied, maximum adsorption (59.7 $\mu\text{g/g}$) was observed in 0.05 mm soil separate of vertisol-2, whereas minimum adsorption of 4.5 $\mu\text{g/g}$ was observed in 2 mm soil of alfisol-1. The amount adsorbed increased with increase in initial concentration and reached a plateau. The isotherms were mainly parabolic in nature with 'S' shaped tendency. The S-shape reflected the initial resistance to the adsorption of herbicides, to overcome later by the cooperative effect of adsorbed molecules. Soil low to medium in organic carbon, has a tendency to give S-shaped isotherms on account of their hydrophilic nature as compared to soil high in organic carbon which tend to be hydrophobic. The adsorption maxima was positively and significantly correlated with organic carbon content. Freundlich ' K_f ' values which indicate the extent of binding of herbicide to the soil constituents were positively and significantly correlated with organic carbon, clay content and clay + organic carbon.

Kew words: Adsorption, Butachlor, Herbicide, Oxadiargyl, Soil particle size

Adsorption is an important process for determining the ultimate fate of organic chemicals in soils because detoxification mechanism such as degradation, metabolism, microbial uptake and mobilization are operative only on the non-sorbed fraction of the molecules. Pesticide sorption refers to the bonding of the chemical to sites on mineral or organic surfaces which controls the quantity of herbicides in soil solution and thus determines its bioavailability and mobility in soil. Pesticide removal through run off is another pathway of removal from crop lands. During runoff events, the clay and silt sized fractions of soil are relatively carried off the field along with the runoff water resulting in the enrichment of these fine sized fractions at the edge of the field. These fine sized fractions are characterized by high specific area and organic carbon content. Pesticide sorption coefficient for these fractions are expected to be much higher than the whole soil.

It has been shown that it is possible to estimate the sorption capacity of different particle size fractions from the knowledge of their organic carbon content and Freundlich constant in a single or limited number of fractions (Karickhoff 1981, Nked-Kizza *et al.* 1983, Shanti *et al.* 1997). Therefore, it is necessary to characterize herbicide sorption not only on whole soil but also on various soil separates. The present investigation was undertaken to characterize the adsorption of technical grade herbi-

cides oxadiargyl (5-tert-butyl-3-[2,4-dichloro-5-(prop-2-nyloxy)phenyl]-1,3,4-oxadiazol-2(3H)-one) and butachlor(N-(butoxymethyl)-2-chloro-N-2,6-(diethylphenyl) (acetamide) on various size particles of four selected soils from the different agro-climatic zones of Andhra Pradesh.

MATERIALS AND METHODS

Experiment was conducted at All India Coordinated Research Programme on Weed Control, Acharya N G Ranga Agricultural University, Hyderabad, with two alfisols (A1: ARS, Anantarakupeta and A2: Karimnagar) and two vertisols (V1: RARS, Lam and V2: 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 (Jackson 1973).

The soil samples were fractionated to 1 mm, 0.5 mm and 0.25 mm by dry sieving sieves. The < 50 μm fraction consisting of silt plus clay was fractionated from these soils by wet sieving method (Jackson 1956). Suitable quantity of soil was suspended in distilled water for 24 h and then stirred on a mechanical stirrer for 30 minutes. The suspension was sieved through 50 micro sieve and the residue was again sieved with fresh amount of distilled water till the filtrate was free of silt plus clay. The filtered suspension was transferred to reagent bottles and

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allowed to stand overnight for settling of silt plus clay and was air dried under shade, pounded and stored for further studies. The procedure used for studying adsorption on soil particle size separates ensured minimal destruction of chemical nature of soil and this procedure was earlier used by Shanti *et al.* (1997) and Nagamadhuri (2003).

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

Two of each 1 mm, 0.5 mm, 0.25 mm and 0.5 mm sieved soils of two selected vertisols and alfisols were equilibrated with 20 ml of oxadiargyl solutions of various concentrations ranging from 0.5, 10, 15, 20, 25, 30 and 35 $\mu\text{g/ml}$ and 0, 10, 20, 30, 40, 50, 60, 70, 80 and 90 $\mu\text{g/ml}$ concentrations of butachlor, respectively in 20 ml capacity bottles for 24 h with intermittent shaking at $27 \pm 2^\circ\text{C}$. Ionic strength was maintained at 0.01 M CaCl_2 . After 24 h, the slurry was centrifuged at 5000 rpm for 15 minutes. In all the adsorption studies 0.01 M CaCl_2 was used as background electrolyte to suppress non-specific adsorption and to simulate natural conditions found in many soils. Further more, it facilitated the separation of solid material from aqueous solution after equilibration (Borggaard Striebig 1998). Identical soil blanks minus the herbicides were maintained. The absorbance for each treatment and the corresponding blank were measured at 226 nm for oxadiargyl and 410 nm for butachlor. The difference was taken as the actual equilibrium absorbance for which the concentration was calculated with reference to the calibration curve. The amount of herbicide adsorbed per gm of soil was calculated from the difference in the initial and equilibrium concentrations. The supernatant was drawn and the oxadiargyl and butachlor concentrations were determined using UV spectrophotometer at 226 and 410 nm and the quantity adsorbed was calculated.

RESULTS AND DISCUSSION

Physico-chemical properties of of vertisol and alfisol revealed low content of organic content in respect of whole soil, which was 0.45 and 0.85 g/ka in alfisol and vetisole, respectively (Table 1). Results revealed that the organic carbon content of 2 mm fraction varied from 3.13 (V_1) to 8.51 g/kg (A_1), 1 mm fractions varied from 4.65 g/kg (A_1) to 9.32 g/kg (V_1); whereas in 0.5 mm fractions organic carbon content varied from 7.12 g/kg (A_1) to 10.86 g/kg (V_1) 0.25 mm fractions 8.86 g/kg (A_1) 11.24 g/kg (V_1) and in 0.05 mm fractions 9.46 g/kg (A_1) to 12.61 g/kg (V_1) (Table 2).

Adsorption of oxadiargyl on soil separates

The adsorption isotherms for various sized fractions were parabolic in nature with S-shaped character indicated a stronger initial competition of water molecules to the surface as compared with the herbicide (Fig. 1 to 4). The extent of adsorption of oxadiargyl (varied in 2 mm sieved soil to 0.05 mm sieved soil in each sample studied) was 4.5 to 11.34 $\mu\text{g/g}$ (V_1); 21.25 to 59.71 $\mu\text{g/g}$ (V_2); 15.36 to 27.65 $\mu\text{g/g}$ (A_2) and 12.04 to 30.34 $\mu\text{g/g}$ (A_1). Among four soils studied, maximum adsorption (59.71 $\mu\text{g/g}$) was observed in 0.05 mm soil separate of vertisol-2, whereas lowest adsorption of 4.5 $\mu\text{g/g}$ was observed in 2 mm soil of alfisol-1. The amount adsorbed increased with increase in initial concentration and reached a plateau. The isotherms were mainly parabolic in nature with 'S' shaped tendency to reach surface saturation in the concentration range studied (Fig. 1 and 2). The data was fitted to Freundlich equation.

Freundlich constants K_f , n and K_{foc} were increased with decreasing particle size fraction. The K_{foc} values for 2 mm sieved soils was less than the obtained for individual soil fractions, while n values were almost similar for all separates. K_f values varied for different size fractions, while n values were quite similar. Similar results were reported by Shanti *et al.* (1997) and Nagamadhuri (2003).

Adsorption of butachlor on soil separates

The extent of adsorption of butachlor was varied in 2 mm sieved soil to 0.05 mm sieved soil in each sample studied was 32.86 to 62.43 $\mu\text{g/g}$ (V_1); 61.63 to 98.61 $\mu\text{g/g}$ (V_2); 57.60 to 99.07 $\mu\text{g/g}$ (A_2); and 35.20 to 59.84 $\mu\text{g/g}$ (A_1). The adsorption isotherms were 'S' shaped (Fig. 3 and 4) confined mainly to the initial stages of adsorption and followed Freundlich adsorption equation.

Freundlich constants K_f , n and K_{foc} were increased with decreasing particle size fraction. The K_{foc} values for 2 mm sieved soils was less than the obtained for individual soil fractions, while n values were almost similar for all separates. The K_f values in 1 mm fractions varied from 0.48 (A_1) to 3.16 (V_1); in 0.5 mm fractions 0.72 (A_1) to 3.81 (V_1); in 0.25 mm fractions 0.91 (A_1) to 4.11 (V_1) and in 0.05 mm fractions 1.16 (A_1) to 4.68 (A_4). The K_{foc} values were also followed the same trend of an increase in the K_{foc} with decrease in soil particle size fraction.

When the amount of herbicide adsorbed per gram of organic carbon was plotted for all the fractions, a single coalesced isotherm was obtained. These values were much closer to K_{foc} and $1/n$ values of the individual fractions, suggesting that organic matter content of soil separates is

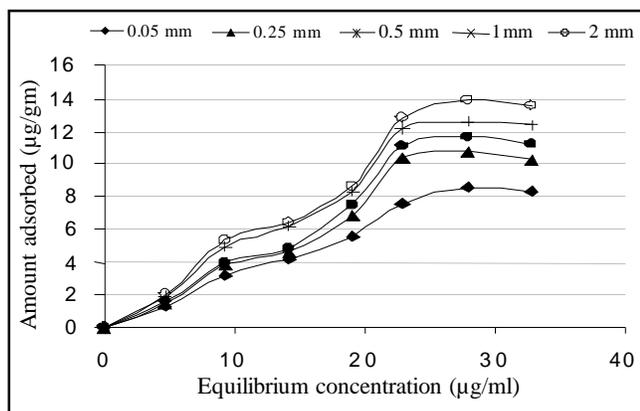


Fig. 1. Adsorption of oxadiargyl in Alfisol-1

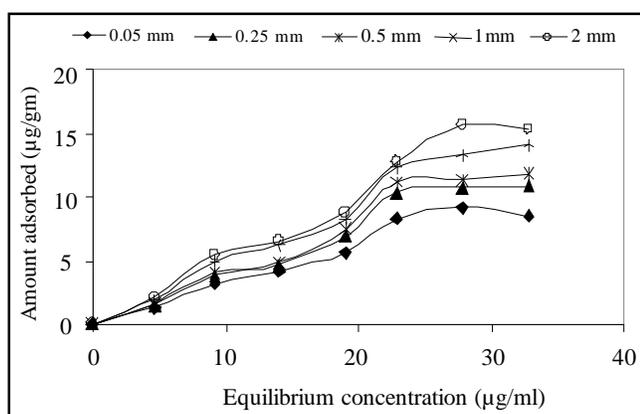


Fig. 2. Adsorption of oxadiargyl in Vertisol-1

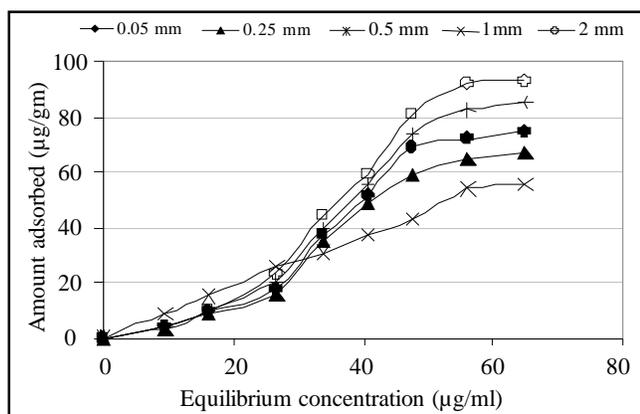


Fig. 3. Adsorption of butachlor in Alfisol-2

responsible for the adsorption of oxadiargyl and butachlor on soils and their particle size separates (Shanthi *et al.* 1997, Nagamadhuri 2003).

Further, it has been shown that it is possible to estimate sorption capacity of different particle size fractions from the knowledge of organic carbon content in a limited or a number of fractions. Similar studies were conducted by Shanti *et al.* (1997) for adsorption of metaxuron and isoproturon; Nagamadhuri (2003) for atrazine and

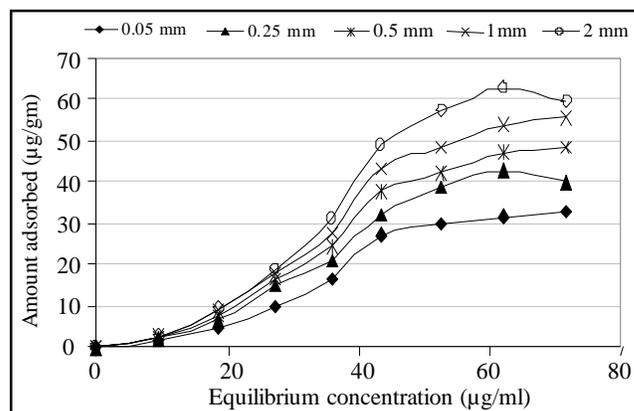


Fig. 4. Adsorption of butachlor in Vertisol-2

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

Soil	pH	EC (dS/m)	OC (g/kg)	Texture (%)		
				Sand	Silt	Clay
<i>Vertisol</i>						
V1: RARS, Lam	7.82	0.22	0.85	55.8	11.0	33.2
V2: Kurnool	8.65	0.29	0.45	84.4	2.00	13.60
<i>Alfisol</i>						
A1: ARS, Anantarajpeta	7.71	0.24	0.67	74.4	3.00	12.60
A2: Karimnagar	6.57	0.16	1.06	76.0	0.4	23.6

Table 2. Organic carbon content (g/kg) in soil separates of selected alfisol and vertisol

Soil/size fraction	2 mm	1 mm	0.5 mm	0.25 mm	0.05 mm
<i>Vertisol</i>					
V1: RARS, Lam	3.13	4.65	7.12	8.86	9.46
V2: Kurnool	5.30	6.60	8.40	9.10	10.30
<i>Alfisol</i>					
A1: ARS, Anantarajpeta	8.51	9.32	10.86	11.24	12.61
A2: Karimnagar	4.53	5.86	7.35	9.64	10.82

isoproturon, Nkedi- kizza *et al.* (1983) for the adsorption of 2,4,5-T and diuron. The organic carbon content increased with decrease in particle size (Table 2). Similar observations were made by Rai *et al.* (2000). It has been shown that herbicides can be removed through run off process, during which the finer sized colloidal fractions are selectively carried off the field with the stream off water. These fine size fractions of soils are characterized by high surface area and organic carbon content. Hence, it is expected that the extent of adsorption on these fractions to be higher than those for whole soils. It is, therefore essen-

Table 3. Correlation coefficients between soil parameters and adsorption of herbicides

Soil parameter	Vertisols		
	K_f	n	K_{foc}
<i>Oxadiargyl</i>			
pH	-0.643	0.204	0.016
OC	0.322	-0.197	-0.070
Clay	0.632*	0.083	0.008
Clay+OC	0.623*	0.076	0.003
<i>Butachlor</i>			
PH	0.829	0.364	0.622
OC	0.099	0.522	0.455
Clay	0.902	0.277	0.565*
Clay+OC	0.901	0.296	0.543*
	Alfisols		
	K_f	n	K_{foc}
<i>Oxadiargyl</i>			
pH	0.122	0.124	0.006
OC	0.290	0.249	-0.136
Clay	0.450	0.044	0.183
Clay+OC	0.460*	0.050	0.182
<i>Butachlor</i>			
PH	-0.385	0.219	-0.401
OC	-0.240	0.283	0.593
Clay	0.886	0.418	0.670
Clay+OC	0.889*	0.416	0.666

tial not only to characterize the extent of adsorption on whole soils but also on various particle size separates of soil.

Correlation coefficients

Simple correlations were worked out between the extent of adsorption, Freundlich constant K_f and k with soil properties. The adsorption maxima (k) was positively and significantly correlated with organic carbon content. The positive and significant correlation between adsorption parameters and clay content indicated the importance of clay content to the adsorption of oxadiargyl and butachlor (Table 3). Another important finding that could be observed was a highly significant and positive correlation between adsorption parameter and clay + OC, indicating that the clay intimated some modifications of their adsorption capacity and they may complement one another on the role of pesticide adsorption beyond that observed in pure inorganic clay systems. Similar results were reported by Raman and Reddy (1993) and Arvind *et al.* (2000). The role of organic carbon in the adsorption of oxadiargyl and butachlor is consistent with reduced biological activity of these herbicides in soils with high organic carbon content. Organic carbon content has been shown to be the first critical parameter positively and significantly correlated with adsorption of above herbicides in soils (Johnson and Sims 1993, Moreau and Mouvet

1997). Clay content of soil is said to be another critical parameter in adsorption of oxadiargyl and butachlor in soils and its role is often masked by that of organic matter and this can become a significant factor when organic carbon content decreases (Arvind *et al.* 2000, Scranio *et al.* 2004). Hitherto, it was opined that organic matter plays an important role in the adsorption of pesticides in soil, where organic matter content exceeds 6 per cent. But in the case of tropical and sub tropical soils, where organic matter content seldom exceeds 2 per cent, clays have been found to be the predominant factor in the adsorption of soil applied herbicides. However, present study revealed that in soils clay and organic matter exists together in the form of clay organo-complexes and these complexes have an important role to play in the adsorption of soil applied herbicides. Raman and Rao (1984) demonstrated that the adsorption of herbicides on model clay-organo complexes was much higher than the corresponding homoionic clays suggesting that the naturally occurring clay-organo complexes in soils play a very significant role in the adsorption of soil applied herbicides. Thus it is possible to obtain significant and positive correlations of adsorption parameters with clay + organic carbon.

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