

## Adsorption-Desorption of Sulfosulfuron on Four Indian Hill Soils

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### ABSTRACT

Adsorption-desorption of sulfosulfuron on four Indian hill soils was studied using batch equilibrium technique. Freundlich constant log K was highest for mollisol-2 soil having low organic carbon, clay content and high pH. Adsorption was in the order inceptisol > mollisol-2 > mollisol-1 > entisol. Sulfosulfuron showed S-type adsorption isotherm curves indicating hydrophilic nature of surface of soils due to which water molecules compete with the herbicide. Sulfosulfuron showed negative hysteresis or irreversible adsorption with hysteresis coefficient values more than 1.

### INTRODUCTION

When a pesticide enters the soil environment, the first process that occurs is adsorption, resulting in distribution into soil adsorbed pesticide and soil-solution pesticide (Gajbhiye and Gupta, 2001). Adsorption is an important process for determining the ultimate fate of organic chemicals in soils because detoxification mechanisms such as degradation, metabolism, microbial uptake and mobilization are operative only on the nonsorbed fractions of the molecules. The extent of adsorption is related to various soil properties, including organic matter content, type and amount of clay, ion exchange capacity and pH (Barriuso *et al.*, 1992). Different pesticides may be adsorbed to very different extents on the same soil (Liu *et al.*, 2002). The adsorption property of different types of soils depends upon the composition of natural colloids in the soil i. e. clay minerals, iron oxides and humic substances. The natural colloids are organomineral associations of multiple soil constituents, which are the main contributors to sorption and transport processes of pesticide and other contaminants in soil and water (Laird *et al.*, 1994).

Sulfosulfuron, a sulfonylurea herbicide chemically known as 1-(4, 6-dimethoxypyrimidin-2-yl)-3-[(2-ethane sulfonyl-imidazo [1, 2-a] pyridine) sulfonyl] urea has been recently introduced by

Monsanto, under trade name Leader. The herbicide is recommended for use in wheat against a broad range of weeds. No much work has been done to study the adsorption-desorption behaviour of the compound. Therefore, studies were undertaken to examine the relationship between sorption and soil variables.

### MATERIALS AND METHODS

Analytical grade sulfosulfuron purity 98.85% was supplied by Monsanto India Limited. Four soils from Tihari-Garhwal region were selected for this study. Surface soil samples from 0-15 cm depth, representative of the areas, were collected. The bulk soil samples were dried in shade, roots and plant remnants were removed, processed by crushing with wooden roller and passed through 36 mesh sieve. The data on physical and chemical properties of soils are presented in Table 1.

Absorption spectra of aqueous solution of sulfosulfuron (10 µg/ml) was recorded in the range of 200 to 350 nm using *Elico-SL-159* UV-VIS spectrophotometer and the  $\lambda_{\text{max}}$  was determined and found to be 209.0 nm. In order to find out the relationship between absorbance and concentration, absorbance of different solutions (0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 µg/ml) of sulfosulfuron in water was recorded at 209 nm wave length using the same

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Table 1. Some general soil properties

Soils	Sand (%)	Silt (%)	Clay (%)	Organic carbon (%)	pH	E. C. (1:2, dSm <sup>-1</sup> )	C. E. C (cmol(p+) kg <sup>-1</sup> )	Iron oxide (%)
Inceptisol	14.50	54.50	31.00	1.58	5.94	0.14	22.35	2.00
Mollisol-1	58.10	29.00	12.90	0.93	6.11	0.13	16.25	1.93
Mollisol-2	32.80	48.20	19.00	1.05	5.86	0.09	18.65	1.96
Entisol	38.10	36.90	25.00	1.31	5.65	0.14	21.45	1.80

spectrophotometer and a calibration curve was plotted between absorbance and concentration.

Equilibration time for the adsorption of sulfosulfuron was determined, using 0.5 µg/ml solution of sulfosulfuron in 0.01 M aqueous CaCl<sub>2</sub>. One gram of the soil sample was taken in 35 ml centrifuge tubes and shaken for different time intervals (2, 4, 6, 12, 24, 36 and 48 h). Equilibration time for sulfosulfuron adsorption on soils was found to be 48 h.

Batch equilibrium experiments were performed to determine adsorption and desorption constants per unit of adsorbent. Appropriate volumes of analytical grade sulfosulfuron were diluted with 0.01 M calcium chloride to get final solutions of concentration 0.5, 1.0, 1.5, 2.0, 3.0 and 5.0 µg/ml. One gram of the air-dried soil sample and 10 ml of each sulfosulfuron (1 : 10 sorbent/solution ratio) were placed in six 35 ml stoppered polypropylene centrifuge tubes and shaken for 48 h. The tubes were incubated at room temperature (25°C) for 24 h for equilibration. After equilibration, the solutions were centrifuged at 3000 rpm for 1 h. The concentration of sulfosulfuron in supernatant liquid was determined, by absorbance at 209 nm, using a spectrophotometer. The difference in pesticide concentration between the initial and final equilibrium solutions was assumed to be due to adsorption. A 0.01 M calcium chloride soil blank was always included and three replicates were analyzed at each pesticide concentration for every soil type used.

To determine the extent of desorption, samples retained after the adsorption studies were shaken with 10 ml of 0.01 M aqueous calcium chloride solution at room temperature for 6 h, then samples were incubated for further equilibration at room temperature for 24 h. Equilibrium dispersions were

centrifuged and the concentration of sulfosulfuron in the supernatant was determined as described previously. Three or four more washings with 0.01 M calcium chloride solution were given and it was observed that no more sulfosulfuron get desorbed. The amount of pesticide that remained adsorbed to the adsorbent was calculated by subtraction.

The adsorption data were fitted to a Freundlich adsorption isotherm model.

$$x/m = KC_c^{1/n}$$

$$\log x/m = \log K + 1/n \log C_c$$

Where,

$x/m$  = amount of isotopuron adsorbed per unit mass of soil (mg/kg)

$C_c$  = equilibration concentration of isotopuron (mg/l)

$K$  and  $n$  = empirical constants

The average distribution coefficient,  $K_d$  was calculated as follows :

$$K_d = (x/m)/C_c$$

Hysteresis coefficient,  $H$ , was calculated for the adsorption-desorption isotherms as follows :

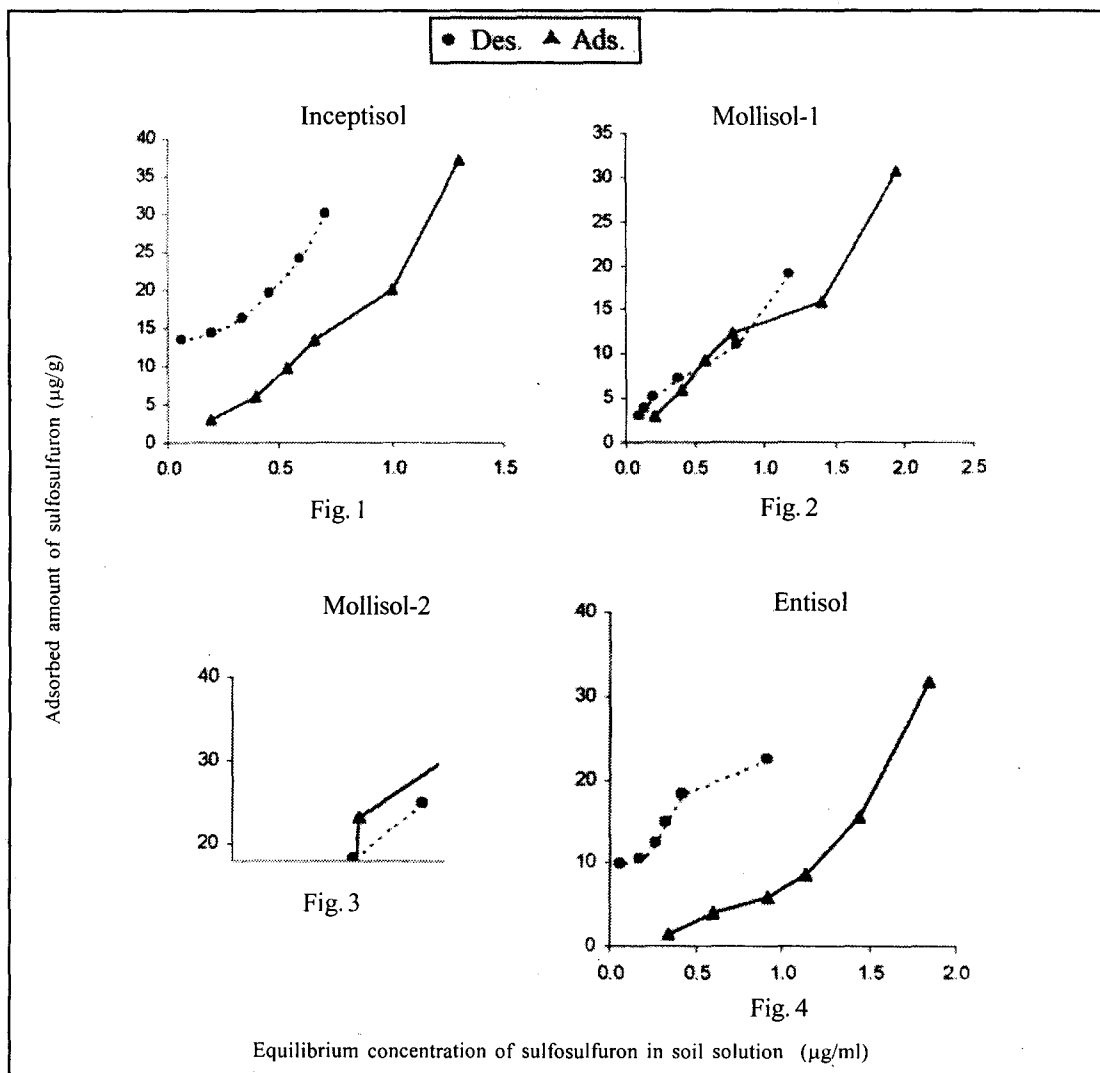
$$H = (1/n / 1/n')$$

Where,  $(1/n)$  and  $(1/n')$  are the Freundlich constants obtained for the adsorption and desorption isotherms, respectively.

## RESULTS AND DISCUSSION

Physico-chemical properties of surface (0-15 cm) soil samples used in the study are presented in Table 1. The UV absorption pattern of 10 µg/ml solution of sulfosulfuron in 0.01 M CaCl<sub>2</sub> was recorded in range of 200-350 nm.

In all the adsorption experiments 0.01 M CaCl<sub>2</sub> was used as background electrolyte to suppress non-specific adsorption and to simulate natural conditions found in many soils. Furthermore, it facilitates the separation of solid material from

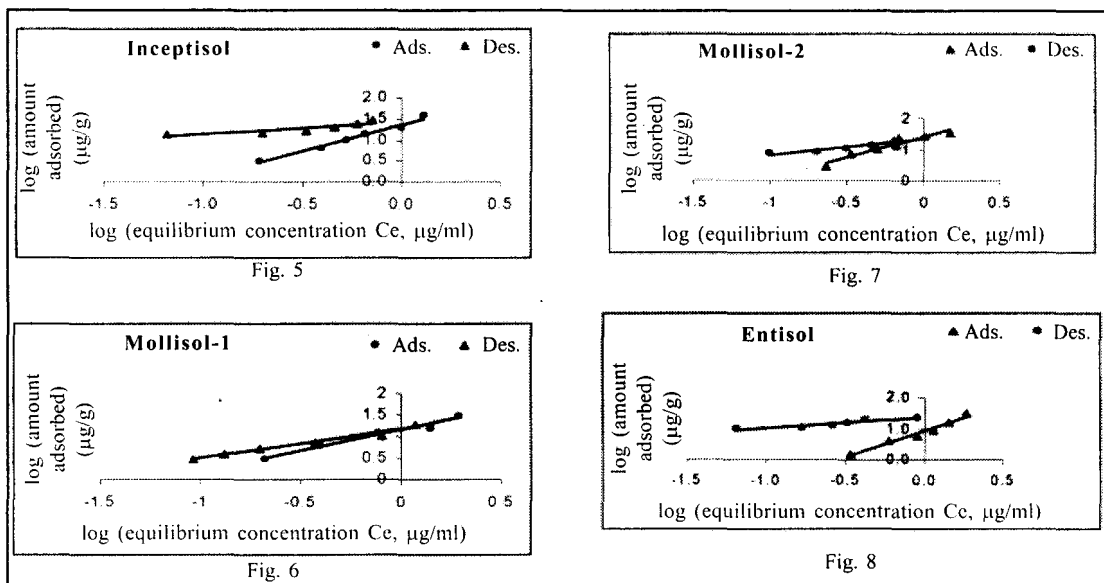


Figs. 1-4. Adsorption-desorption isotherms of sulfosulfuron on soils.

aqueous solution after equilibration (Borggaard and Streibig, 1988). The plots of adsorbed amount of sulfosulfuron per unit mass of soil versus the equilibrium concentration of sulfosulfuron in solution for different soils are shown in Figs. 1 to 4. With the increase in initial concentrations of sulfosulfuron from 5.0 to 50.0 µg/g soil, the adsorption increased from 61.7 to 74.04% in inceptisol, 57.8 to 61.2% in mollisol-1, 53.6 to 70.08%

in mollisol-2 and 31.2 to 63.8% in entisol soil.

The adsorption isotherms in case of mollisol-1, inceptisol, mollisol-2 and entisol soils were of 'S' type (Giles *et al.*, 1960). These types of isotherms are characteristic of the strong competition between water molecules and the pesticide for the adsorption sites at low pesticide concentration and or molecular interaction between the sorbed species. Adsorption becomes easier as the concentration of sulfosulfuron



in the aqueous phase increases. The 'S' type adsorption isotherms might be due to the hydrophilic nature of surface of soils due to which water molecules compete with the herbicide till a certain level of herbicide is built up. Morrica *et al.* (2000) reported 'S' type isotherm for adsorption of imazosulfuron on soils.

The constants of Freundlich equation  $\log K$  and  $1/n$  alongwith coefficient of determination ( $r^2$ ) for linear fits,  $K_d$  values and distribution coefficient normalized for the organic carbon content  $K_{oc}$  are given in Table 2. The plots of Freundlich adsorption isotherm of sulfosulfuron for different soils are shown in Figs. 5 to 8.

The  $\log K$  values in decreasing order for different soils are Mollisol-2 (1.40) > Inceptisol (1.35) > Mollisol-1 (1.16) > Entisol (0.93). The Freundlich isotherms had slopes ( $1/n$ ) ranging from 0.98 to 1.68 with the maximum value noted in entisol and minimum in mollisol-2. The values of  $1/n$ , very close

to unity, indicated as straight line relationship between pesticide concentration and adsorption.

A significant negative correlation between  $1/n$  and soil pH indicated that as the soil pH increased, the slope factor decreased or the sites of adsorption tended to become saturated and adsorption intensity decreased (Table 3). In general, the decrease in absorption at increased pH could be attributed to increase in negative charge on soil colloids. Such behaviour is commonly observed for adsorption of weakly acidic compounds on mineral surface of soils around pH (pzc) (pH value of the solution when the total net particle charge vanishes and is sometimes also called as isoelectric point) as the anionic form of the pesticide adsorbed on pH dependent positive sites on soil minerals. With decreasing pH, the positive surface charge is increased as the soil mineral surface hydroxyls are protonated according to the reaction  $>S-OH + H^+ \rightarrow S-OH_2^+$ , which facilitates adsorption of negatively

Table 2. Freundlich adsorption-desorption parameters

Soils	$\log K$	$1/n$	$r^2$	$K_d$	$\log K'$	$1/n'$	$K_d'$	HI
Inceptisol	1.35	1.27	0.9825	19.84	1.43	0.31	75.38	4.13
Mollisol-1	1.16	0.98	0.9711	14.66	1.17	0.67	22.83	1.47
Mollisol-2	1.40	1.36	0.9253	21.38	1.34	0.54	37.61	2.51
Entisol	0.93	1.68	0.9644	6.01	1.34	0.34	61.52	4.95

Table 3. Simple correlation coefficients (r) between soil properties and two surfaces Freundlich adsorption-desorption parameters of sulfosulfuron in different soils

Soil property	log k	1/n	log k'	1/n'	HI	Kd	Kd'	Koc
Sand (%)	-0.47	-0.37	0.97*	0.800	-0.620	-0.404	-0.85	-0.47
Silt (%)	0.69	0.221	0.89	-0.597	0.39	0.633	0.664	0.693
Clay (%)	0.07	0.53	0.93	-0.969*	0.859	0.004	0.994	0.069
O. C. (%)	0.047	0.419	0.87	-0.944	0.818	-0.007	0.98*	0.047
pH (1 : 2)	0.46	-0.998**	-0.52	0.658	-0.815	0.536	-0.520	0.460
E.C. (1 : 2, dSm <sup>-1</sup> )	-0.59	0.070	0.079	-0.486	0.497	-0.580	0.506	-0.591
C. E. C. [cmol(p <sup>+</sup> ) kg <sup>-1</sup> ]	-0.072	0.67	0.916	0.996**	0.937	-0.145	0.989*	-0.072
Fe oxide (%)	0.93	-0.65	0.204	0.159	-0.437	0.940	-0.006	0.930

charged acidic molecules and results in the increased adsorption with decreasing pH (McBride, 1994).

The Kd values revealed that there was moderate to high adsorption in four tests soils. In all the soils, the average Kd values were greater than one, showing that the sulfosulfuron molecules had much greater affinity to soil particles than to soil solution. The Kd values showed positive and significant correlation with clay, CEC and organic carbon content. 1/n' showed a negative and significant correlation with CEC. So, it is not easy to desorb sulfosulfuron from the soil having high clay, CEC and organic carbon content.

Here all the soils have HI values greater than 1. The parameter HI is hysteresis coefficient. When HI is more than 1, negative hysteresis or irreversible adsorption is observed (Barriuso *et al.*, 1994). Negative hysteresis in the soils is observed due to solid concentration effect (Perlinger *et al.*, 1993).

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