



## Adsorption–desorption of atrazine on vertisols and alfisols

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### ABSTRACT

Adsorption–desorption of atrazine was measured in four soils of Hyderabad using batch equilibrium method at  $27\pm 1^\circ\text{C}$ . The Freundlich equation was used to describe batch results. Both adsorption and desorption isotherms were well described by the Freundlich model. Fitted  $K_f$  value for desorption isotherms were consistently higher than those associated with adsorption. The opposite trend was observed for the exponential parameter  $n$ . The results revealed that the desorption data deviated significantly from adsorption data. The deviation, which is commonly referred to as hysteresis, was more prominent with higher adsorbed concentration of atrazine and incubation time. Desorption was significantly higher at the lowest adsorbed level of atrazine. The Freundlich  $K_f$  and  $n$  values were higher than that for adsorption and increased with increase in initially adsorbed concentration of atrazine.

**Key words:** Adsorption, Alfisols, Atrazine, Desorption, Vertisols

Adsorption–desorption processes are necessary in understanding herbicide retention behaviour and its potential mobility within the soil. Atrazine can be released from soil adsorption sites when its concentration in the solution phase decreased due to dilution, volatilization or translocation. This process is called desorption and can be initiated by diluting or replacing the soil solution with atrazine free solutions (Clay and Koskinen 1990a, Ma *et al.* 1993). Batch equilibration has been extensively used in several investigations. The Freundlich model is a commonly used approach describing atrazine distribution between soil and solution for both sorption processes. However, the fitted  $N$  is consistently lower and  $K_f$  is higher than that obtained from adsorption isotherms (Clay and Koskinen 1990a, b, Ma *et al.* 1993, Stechouwer *et al.* 1993, Laird *et al.* 1994). Therefore, less herbicide is desorbed from soils than predicted by the adsorption isotherm, which is often referred to as hysteresis.

Several factors such as organic matter content, soil pH, extracting solvent, temperature and incubation time, influenced the amount of atrazine adsorbed and desorbed in soil. Hysteresis is more obvious under low soil pH, long reaction time, high organic matter content, frequent drying and wetting and high degradation rates (Clay and Koskinen 1990a, Pignatello and Huang 1991). Laird *et al.* (1994) reported that extensive hysteresis resulted from

atrazine adsorption on organic components, while little or no hysteresis was observed for clay minerals. Adsorption–desorption properties of atrazine can be directly related to their mobility in soil and thus, predict their movement to ground water. There is increasing evidence that some fraction of most pesticides is irreversibly bound on adsorption sites in soils (Khan 1982). Hence, a detailed study of atrazine adsorption–desorption phenomenon on two soils was conducted.

### MATERIALS AND METHODS

One sample each from vertisol and alfisol of ANGRAU campus, Rajendranagar and other two samples from vertisol and alfisol of ICRISAT, Hyderabad were selected for the study. The samples were analyzed for physico-chemical properties using standard procedures (Table 1). Technical grade atrazine (>95% purity) obtained from M/S Rallis India Ltd. was used. Atrazine (2-chloro-4 ethyl amino-6-isopropyl amino-1-3, 5 traizine) is a soil and foliar applied pre- and post- emergence herbicide used for the control of broad-leaved weeds in sorghum, maize, sugarcane and other cereals.

Adsorption was studied by equilibrating 5 g of 0.25 mm sieved soil with 20 mL of aqueous solutions containing 0 to 50 mg/mL atrazine in 0.01 M  $\text{CaCl}_2$  for 24 hr at  $27\pm 1^\circ\text{C}$  and centrifuging at 4,000 rpm for 15 minutes. Identical soil blanks without atrazine were maintained as control. The equilibrium concentration of atrazine was determined spectrophotometrically at 221 nm with respect to standard curve, after correcting for soil blanks.

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Desorption was studied using batch equilibration followed by replacing the supernatant with 0.01 M CaCl<sub>2</sub>. Five grams of 0.25 mm sieved soil samples were taken and treated with atrazine solution containing 0 to 50 mg/mL and 0.01 M CaCl<sub>2</sub>. After incubating for 2 hr at 27±2°C, the slurry was centrifuged at 2000 rpm for five minutes and 5 mL of the supernatant was taken out and its absorbance was measured at 221 nm. The volume of the remaining slurry was made up again to 20 mL by adding 5 mL of 0.01 M CaCl<sub>2</sub> solution, equilibrated against for five consecutive days. The same operations were carried out simultaneously with soil blanks and corrections were applied at every stage. The amount of atrazine desorbed and the amount remaining adsorbed on the successive days were calculated and isotherms were drawn. The amount desorbed was calculated using

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

where C<sub>o</sub><sup>n</sup> is initial concentration of atrazine on nth day, C<sub>e</sub><sup>n-1</sup> is equilibrium concentration on (n-1)th day. Amount desorbed on nth day is given by (C<sub>e</sub><sup>n</sup> - C<sub>o</sub><sup>n</sup>) x 20.

**RESULTS AND DISCUSSION**

-Adsorption-desorption isotherms for selected soils are given (Fig. 1-4). The adsorption isotherms were found to be mainly parabolic in nature with S-shaped curvature mainly confined to initial stages of adsorption. The tendency for S-shaped character indicated a stronger initial competition of water molecules to the adsorbent as compared to the herbicide, till a certain level of adsorbed herbicide is built up. This is a common feature for the adsorption of organic chemicals on the soils of low organic matter or on clay (Raman and Rao 1987). The adsorption data was described by Freundlich equation and the constants K<sub>f</sub> and n are given in Table 2.

K<sub>f</sub> value was high for soil V2, which was due to high organic carbon content. The resistive effect of organic matter on adsorption of pesticide is well established (Graham and Khan 1992, Ma *et al.* 1993, Raman and Reddy 1993, Rocha and Walker 1995).

Desorption isotherms for every level of initial concentration of added atrazine in both the soils did not coincide with adsorption isotherms (Fig. 1-4). The slope of

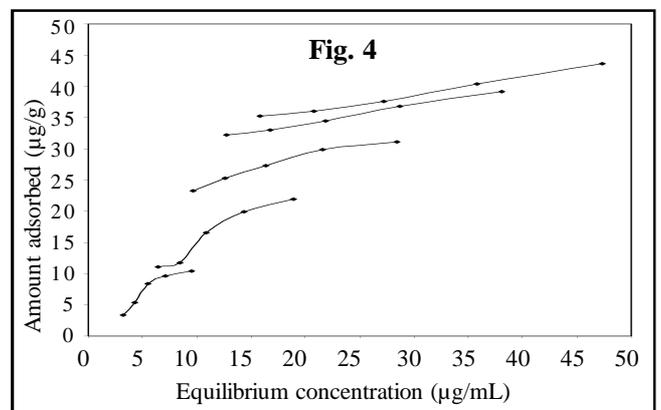
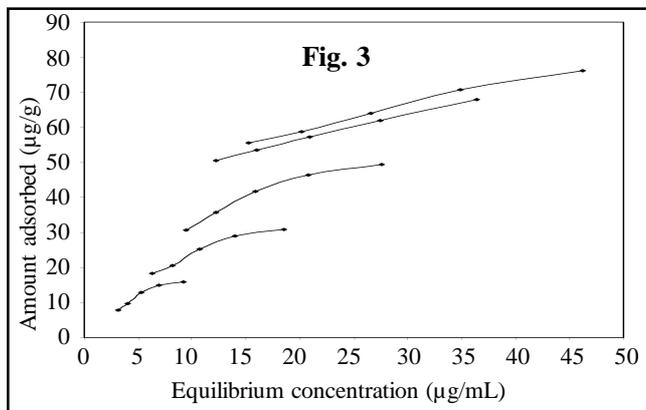
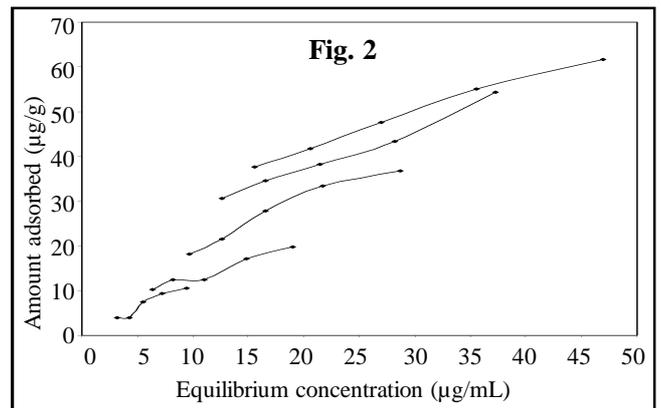
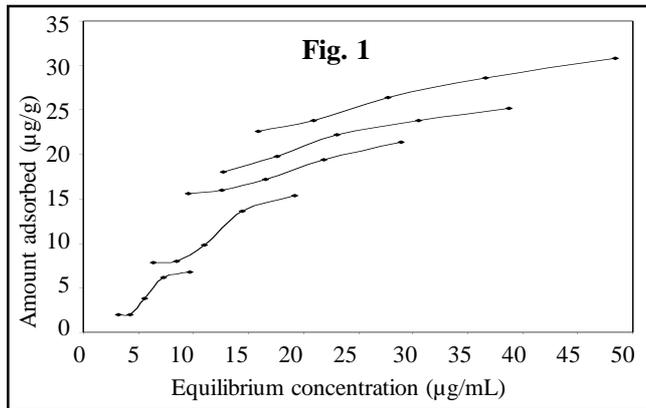


Fig. 1-4. Adsorption-desorption isotherms of atrazine on vertisols and alfisols

**Table 1. Physico-chemical properties of selected soils**

Soils	pH	EC (dS/m)	Organic C (g/kg)	Mechanical composition (%)			Texture
				Sand	Silt	Clay	
V <sub>1</sub> (College farm ANGRAU, Hyderabad)	7.32	0.61	0.53	30.0	41.8	28.2	Silty clay loam
V <sub>2</sub> (ICRISAT, Hyderabad)	6.99	1.44	1.17	18.8	46.2	35.0	Silty clay loam
A <sub>1</sub> (College farm ANGRAU, Hyderabad)	7.03	0.19	0.09	69.4	18.6	12.3	Loamy sand
A <sub>2</sub> (ICRISAT, Hyderabad)	6.67	0.53	0.37	75.6	6.2	18.2	Loamy sand

**Table 2. Freundlich constants for adsorption of atrazine on vertisols and alfisols**

Soil	V <sub>1</sub>	V <sub>2</sub>	A <sub>1</sub>	A <sub>2</sub>
Organic carbon (g/kg)	0.53	1.17	0.09	0.37
K <sub>f</sub>	2.66	4.08	1.81	2.41
N	1.13	1.02	0.83	1.08

K<sub>f</sub> and n are Freundlich constants

isotherms for desorption was obtained by desorbing the herbicide adsorbed at the initial concentrations. The slope of desorption isotherm was much less than the slope for adsorption isotherm and less amount of herbicide was present in equilibrium solution than during adsorption. The results indicated that desorption isotherm deviated significantly from the adsorption isotherms. Such a deviation between adsorption and desorption isotherm is referred to as hysteresis. Hysteresis is often observed in pesticide adsorption-desorption studies with soil (Koskinen and Harper 1990, Ma *et al.* 1993, Reddy *et al.* 1995, Mersie and Seybold 1996, Jenks *et al.* 1998).

The hysteresis was more pronounced when desorption was carried out from higher levels of adsorbed atrazine. Thus, when desorption was carried out from soils where less amount of atrazine was present, the desorption isotherms were very close to the adsorption isotherms. This showed that the degree of irreversibility increased with increase in sorbed atrazine.

Percent desorption in both the soils decreased with increase in the amount initially adsorbed (Table 3). The desorption from the lower levels of concentration was significantly higher in both the soils, from the other levels of concentration. The percent desorption was more in alfisols than vertisols in the order of A<sub>2</sub> > A<sub>1</sub> > V<sub>1</sub> > V<sub>2</sub>, which was in the order of decreasing organic carbon of the soils. The significant variation in cumulative desorption between all the soils at different levels of initial concentration of atrazine could be due to the fact that soil is a heterogeneous entity with sorptive sites that vary widely in the type and energy of binding.

In the present study, it was found that the desorption isotherms were also of Freundlich in nature and similar to those obtained by Seybold and Mersie (1996), Graham

**Table 3. Cumulative desorption of atrazine in five consecutive days in vertisols and alfisols**

Initial concentration (µg/mL)	Per cent desorbed in five days			
	V <sub>1</sub>	V <sub>2</sub>	A <sub>1</sub>	A <sub>2</sub>
10	62.82	50.30	70.59	67.31
20	58.58	41.09	68.83	63.01
30	50.00	38.06	63.55	57.87
40	43.75	29.50	60.32	51.10
50	38.96	27.03	53.90	48.17

and Khan (1992), Moreau and Mouvet (1997) and Benoit *et al.* (1999). The constants K<sub>f</sub> and n for desorption were calculated and are given in Table 4.

The Freundlich K<sub>f</sub> values for the desorption isotherms were found to increase with increasing initial concentrations of atrazine in both the soils. Similar results were reported by Ma *et al.* (1993), Pignatello (1989) and Gan *et al.* (1996). Larger K<sub>f</sub> values for adsorption than desorption indicate stronger binding of atrazine to soils (Reddy *et al.* 1995).

The extent of hysteresis was more pronounced as the incubation time increased and indicated that atrazine recovery decreased with incubation (Ma *et al.* 1993) for atrazine desorption. It is generally accepted that the rate of desorption is slower than rate of adsorption (Calvet 1989).

The higher clay content, organic C content and CEC of clay loam soils (V<sub>1</sub> and V<sub>2</sub>) compared to loamy sand (A<sub>1</sub> and A<sub>2</sub>) may be the factors that are responsible for increased amounts of non-desorbable atrazine on clay loam. These results are in conformity with the results reported earlier by Ma *et al.* (1993), Seybold *et al.* (1994), Gan *et al.* (1996) and Reddy *et al.* (1997). The values of K<sub>f</sub> and n however, may not have the same physical significance as in adsorption isotherms because a part of the soil applied pesticide has often been shown to become bound and unextractable by water or even by organic solvents (Khan 1980, 1982). Ideally, K<sub>f</sub> and n for desorption isotherms should be similar to those for adsorption isotherms, if the non desorbable portion at each step is known and is compensated for. This is unfortunately not possible. The

**Table 4. Freundlich  $K_f$  and  $n$  values for desorption of atrazine from selected vertisols and alfisols**

Soils	10 µg/mL		20 µg/mL		30 µg/mL		40 µg/mL		50 µg/mL	
	$K_f$	$n$								
V <sub>1</sub>	1.06	0.86	2.34	1.25	6.83	1.33	9.44	1.37	10.19	1.38
V <sub>2</sub>	2.28	1.36	4.89	1.21	10.42	1.27	11.16	1.31	13.17	1.32
A <sub>1</sub>	0.42	1.05	1.77	0.90	3.18	1.11	5.81	1.28	7.18	1.26
A <sub>2</sub>	0.66	1.11	2.01	1.08	5.16	0.98	6.33	1.09	9.07	1.11

increasing  $K_f$  values with increasing adsorbed concentration is indicative of increasingly difficult desorption.

The main cause of hysteresis, during desorption was the presence of a number of heterogeneous adsorbing sites of varying energy levels on soils. In addition to this, are the modifications that take place in the soil itself during adsorption-desorption process (Calvet 1980). Desorption of atrazine from both vertisols and alfisols was hysteric. The adsorption of herbicides and their consequent desorption is not a single valued relationship, hence, a portion of adsorbed herbicide is resistant to desorption. Degradation of parent compound may have occurred during equilibrium and also by physical adsorption/or chemical properties of soil solution system (Cheng 1990). As the herbicide degrades, a new equilibrium is established with more parent compound being removed from solution and bound to soil. Changes in solution composition during desorption might have occurred. Soluble soil organic carbon decreased when 0.01 M CaCl<sub>2</sub> was used for desorption replacement solution. Also, the herbicide may be bound to replicated soil sites and not have been readily released into solution (Clay and Koskinen 1990a). Repeated centrifugation of the slurry in batch equilibration has been reported to be partly responsible for hysteresis observed in some pesticides (Bowman and Sans 1985).

Ma *et al.* (1993) suggested two possible mechanisms responsible for reversible or irreversible atrazine adsorption in soils. One was due to the formation of atrazine soil complexes that are not easily desorbable into soil solution. In fact, atrazine can strongly bound to soil organic matter by either chemical or physical means other mechanisms include chemical and microbial degradation of atrazine. Further with increasing amount of adsorbed pesticide not only the surface sites are occupied but the pesticides may find its way into soil micropores caused by clay and structurally complex polymer net work. Thus, rediffusion of herbicide into soil solution becomes hindered due to tortuosity of the pores followed by the unfavorable energetics (Pignatello 1989, Raman and Patnaik 1993).

In the present investigation, extent of hysteresis during adsorption-desorption of atrazine on both vertisols and alfisols was quantified. A portion of observed hysteresis with atrazine on vertisols and alfisols could be a result of soil bound desirable parent herbicide or degradation products. The amount of non-desorbable atrazine and the amount of hysteresis accounted for in this study were dependent on soil type, solvent used for extraction, repeated centrifugation of slurry and irreversible conjugation of atrazine with soil organic compounds and observed hysteresis may be due to change in soil structure-ionic strength and dissolved organic carbon content of the solution phase during desorption process (Barriuso *et al.* 1992, Wang *et al.* 1992). However, the amount of non-desorbable herbicide may explain a portion of observed hysteresis during laboratory batch desorption experiments.

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