

Research Article

Sorption Behaviour of Metribuzin in Tomato Growing Soils

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Abstract

Metribuzin is a triazinone herbicide used as pre and post emergence to control annual grasses and broadleaf weeds in the field and vegetable crops. Adsorption of herbicide on soil directly or indirectly controls the fate of herbicide, including movement in soil. This experiment was conducted to study the sorption behavior of metribuzin in three different tomato growing soils in Telangana state of India. Physical and physico chemical properties of the soil highly influenced the sorption of metribuzin. Organic carbon and clay content of the soil exhibited significant positive correlation with adsorption. Adsorption isotherms were found to be best fitted with Freundlich equation. The K_f (Freundlich adsorption coefficient) values were 0.062 to 0.729.

The desorption K_f values varied between 0.988 ($10 \mu\text{g mL}^{-1}$) to 7.930 ($50 \mu\text{g mL}^{-1}$) in S-1; 0.019 ($10 \mu\text{g mL}^{-1}$) to 0.385 ($50 \mu\text{g mL}^{-1}$) in S-2 and 0.237 ($10 \mu\text{g mL}^{-1}$) to 2.930 ($50 \mu\text{g mL}^{-1}$) in S-3. Desorption isotherms of soil adsorbed metribuzin showed hysteresis, which was more when the desorption was carried out from higher initial concentrations of herbicide solution.

Keywords: Metribuzin, Adsorption, Desorption, Freundlich adsorption coefficient, Hysteresis

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Introduction

Metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one], is an asymmetrical herbicide of triazinone group and it is one of the most-widely used selective herbicides for pre and post-emergence control of annual grasses and broadleaf weeds in the field (sugarcane, maize) and vegetable crops (potato, tomato, carrot). In Telangana state, metribuzin is one of the most popular herbicide used in tomato crop as post-emergence herbicide for the broad-leaf and grass weed control by farmers. Consumption of metribuzin in Telangana and Andhra Pradesh has increased from 15 tons/year (2008-09) to 85 tons/year (2013-14) [1].

Herbicides applied to the soil are subjected to physico-chemical, chemical and microbial processes which will decide fate of the herbicide in the environment. Fate of the herbicide in the soil influence the bio-availability, movement of the herbicide and its environment contamination potential. Among the physico-chemical processes that influence the fate of herbicide, adsorption and desorption, persistence, movement and leaching have been found to be predominant processes in most agricultural soils. Adsorption-desorption is a surface phenomena which directly and indirectly controls the effect of magnitude of other processes. The extent of herbicide adsorbed is determined by soil properties such as organic carbon, nature and amount of clay, pH and CEC. Desorption on the other hand refers to the amount of herbicide desorbed from the soil consequent to the adsorption and indicate the amount of herbicide available to target plant species. Sorption of soil-applied herbicide can be influenced by soil solution characteristics, thus application of fertilizers affect the sorption and mobility of herbicide [2-4]. Many researchers [5-8] have indicated that soil organic carbon content is largest single factor responsible for metribuzin sorption in soils. Freundlich isotherms were used by [9] to study the adsorption of metribuzin and their results showed that as per the shape of the isotherms adsorption was not linear and decreases at higher concentrations. Rigi *et al.* (2015) [10] indicated that the adsorption isotherms of metribuzin were well described by the Freundlich equation.

As there is no data published on the sorption behavior of metribuzin in different tomato growing soils of Telangana state, this experiment was conducted to study the adsorption desorption characteristics and the influence of soil properties on sorption behavior of metribuzin in these soils.

Experimental

Adsorption – desorption studies were carried out in three selected samples with widely varying soil characteristics and having no metribuzin residues. Soil samples were collected from farmer's fields at three different locations in Ranga Reddy district of the Telangana state considering the soil properties. At each selected location, composite soil samples were collected at different spots from a depth of 0-15 cm, quartered and about 1.0 kg of each soil sample was brought to the laboratory, air dried under shade and processed by passing through a 2 mm sieve. These samples were analysed for their physical and physico-chemical properties. Soil pH was measured in 1:2.5 soil-water suspension with a glass pH electrode, the soluble salt content of the soil was estimated by determining the electrical conductivity in 1:2.5 soil water extract (after stirring for half an hour) using EC bridge and was expressed as dS m^{-1} (Jackson, 1973) [11]. The organic carbon content was determined by wet digestion method of Walkley and Black (1934) [12] as described by (Jackson, 1973) [11] and expressed in per cent. CEC was determined by the ammonium acetate method [13], soil particle fractions were determined by the Bouyoucos hydrometer method [14]. Physico-chemical properties of the three tomato growing soil samples are presented in the **Table 1**.

Table 1 Physico –chemical properties of soil samples

S No	pH	EC (dS m^{-1})	CEC $\text{mol(p+)} \text{ kg}^{-1}$	OC (Mg/m^3)	Particle size distribution (%)			Texture
					Clay	silt	sand	
S-1	8.84	0.27	31.3	0.94	43.7	30.2	26.1	Clay
S-2	6.52	0.13	13.91	0.32	15.8	13.5	70.7	Sandy loam
S-3	8.17	0.42	24.2	0.47	31.1	34.2	34.7	Clay loam

Characteristics of Herbicide (metribuzin)

Analytical grade metribuzin (99% purity) was obtained from Dr. Ehrenstrofer GmbH, Germany and used for present study for preparation of standards without any further purification. Metribuzin standard solution of 50 mg/kg was prepared in methanol and used as stock solution. Aliquots from this stock solution were diluted to prepare desired concentrations (0.001 to 2.0 mg kg^{-1}).

Adsorption-desorption experiments

Adsorption experiment with the collected soil samples was carried out adopting the batch equilibrium protocol. Batch equilibrium technique is the most commonly used method to characterize adsorption – desorption. [15-16]. Soil (five grams) was equilibrated with 20 mL of metribuzin solutions of various concentrations ranging from 0 to 50 $\mu\text{g mL}^{-1}$ for 24 hours with intermittent shaking at constant temperature of 27 $^{\circ}\text{C}$. CaCl_2 of 0.01M concentration was used to maintain the ionic strength. After 24 hours, the slurry was centrifuged at 4,000 rpm for 15 minutes. Identical soil blanks were maintained (without addition of herbicide). The absorbance for each treatment and corresponding blank values were measured at 455 nm. The difference between the treatment and blank was taken as actual equilibrium absorbance for which the concentration was calculated with reference to the calibration curve. Using the difference between initial and equilibrium concentration the amount of herbicide adsorbed per gram of soil was calculated.

Desorption studies were also conducted on the same soil. Five grams of 2.0 mm sieved soil was taken and treated with 20 mL of metribuzin solution containing 0, 10, 20, 30, 40 and 50 $\mu\text{g mL}^{-1}$ of 0.01 M CaCl_2 . The samples were incubated for 24 hrs and then the slurry was centrifuged at 2000 rpm for five minutes, from that 5 mL of the supernatant was used for measuring the absorbance. By adding 5 mL of 0.01 M CaCl_2 to the remaining 15 mL the volume and made to 20 mL. The mixture was again shaken well and incubated for 24 hrs and centrifuged at 2000 rpm to determine equilibrium concentration. Identical blanks were maintained simultaneously. This process was repeated for five consecutive days. The adsorption – desorption experiment was carried out in quadruplicates. The amount of herbicide desorbed was calculated as follows:

$$C_0^n = C_e^{n-1} \times 15/20$$

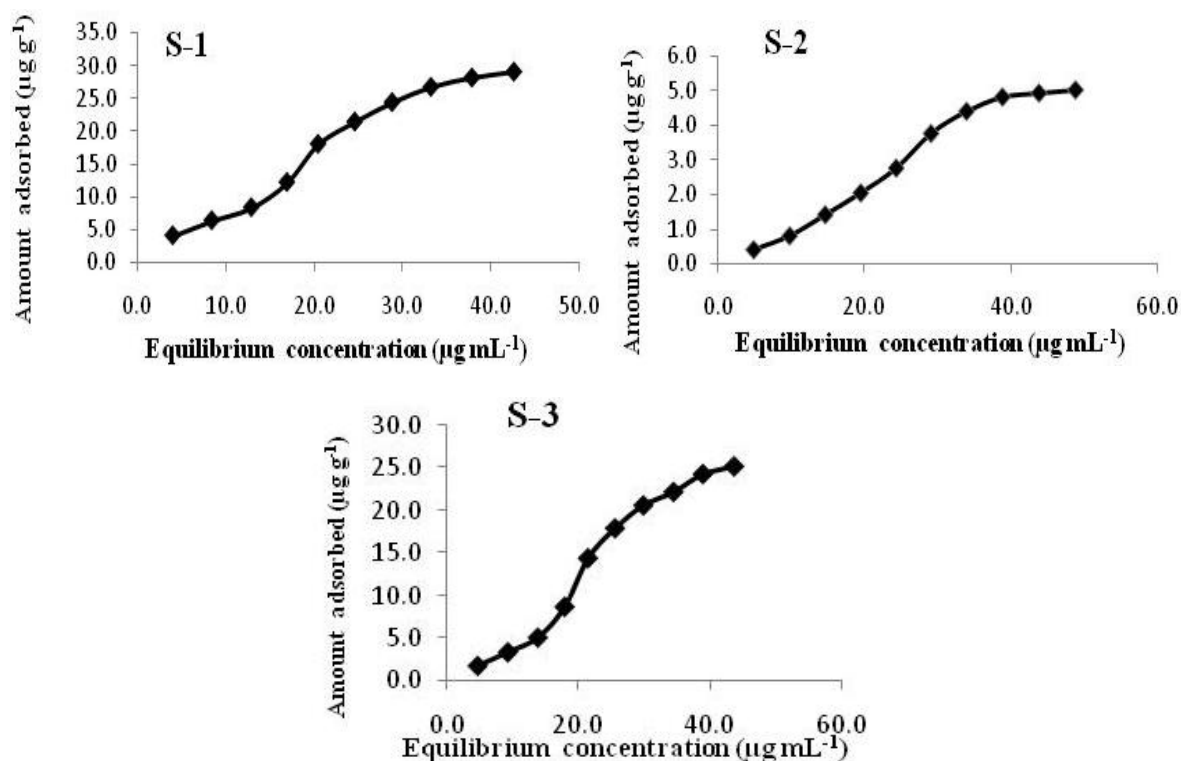
Where, C_0^n = initial concentration of metribuzin on nth day, $C_e^{(n-1)}$ = equilibrium concentration on (n-1)th day

The data obtained from studies on adsorption of metribuzin on 2 mm sieved soils, and adsorption - desorption was subjected to mathematical analysis using adsorption isotherms. The adsorption isotherms were constructed using the

amount adsorbed ($\mu\text{g g}^{-1}$) on Y-axis and equilibrium concentration ($\mu\text{g mL}^{-1}$) on X-axis.

Results and Discussion

Adsorption isotherms were calculated for metribuzin by using the batch equilibration method. Adsorption isotherms were plotted by taking adsorbed herbicide on soil on Y-axis against the equilibrium concentration on X-axis. Metribuzin showed maximum absorbance in visible range at 455 nm wavelength. The adsorption was slower at the lower initial concentrations ($<15 \mu\text{g mL}^{-1}$) and increased rapidly at the intermediate concentrations and tended to slow down at higher concentrations of $>40 \mu\text{g mL}^{-1}$. The adsorption data fitted well with Freundlich equation. The Freundlich parameter K_f , obtained as the intercept and $1/n$ the slope of the isotherm were calculated by plotting log values of the equilibrium concentration and amount of metribuzin adsorbed on the soils. The adsorption isotherms were mainly parabolic in nature with 'S' shaped character in all three soil samples. Adsorption isotherms of these soil samples were presented in **Figure 1-3**.



Figures 1-3 Adsorption isotherms of selected soil samples (S-1), (S-2) and (S-3)

The Freundlich constants K_f , 'n' and (Soil-water distribution quotient) K_d , (Soil organic carbon- water distribution coefficient) K_{doc} for the tomato growing soils are presented in the **Tables 2** and **3**. The K_f values for the soils were 0.729 (S-1), 0.062 (S-2) and 0.209(S-3) the n values were 1.01 (S-1), 0.85 (S-2) and 0.76(S-3). 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. The K_f values computed in the study are closely correlated to the value proposed by the [17] Footprint PPDB (2001) for metribuzin and also to the range of K_f values mentioned in the EU certification records that range from 0.018 to 1.9. Further, the K_f values reported by Johnson and Pepperman (1995) [18] and Lagath *et al.* (2011) [19] are in the range of K_f coefficients for metribuzin obtained in the present study.

Table 2 Freundlich constants K_f , n and K_{foc} and K_d , K_{doc} values for adsorption of metribuzin on soil samples

S. No.	OC %	K_f	N	K_{foc}	K_d	K_{doc}
S-1	0.94	0.729	1.01	77.34	0.70	74.64
S-2	0.32	0.062	0.85	19.37	0.11	35.48
S-3	0.47	0.209	0.76	44.38	0.60	127.10

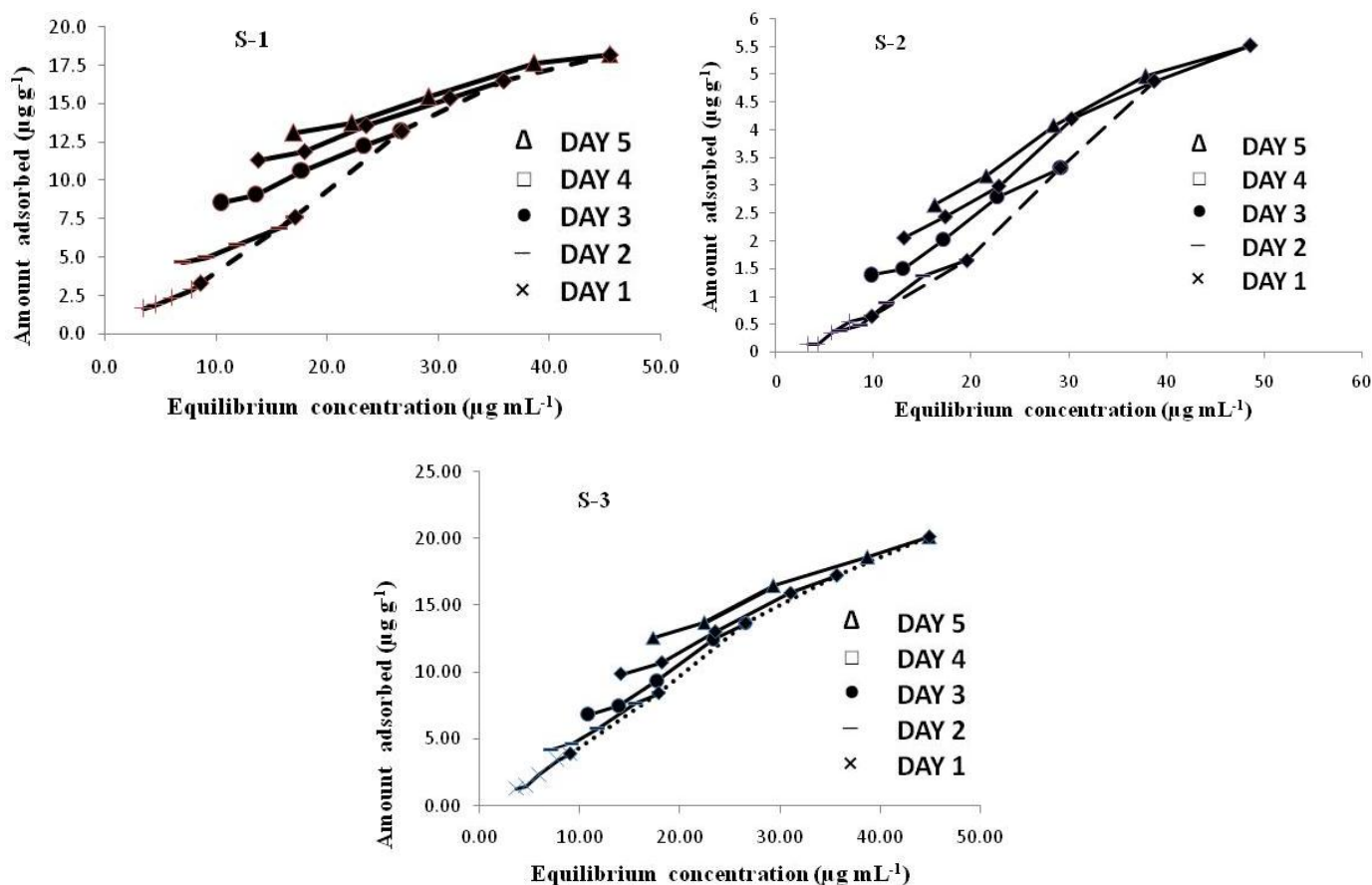
Table 3 Freundlich constants for adsorption desorption of metribuzin from selected soil samples

Soil No.	10 $\mu\text{g mL}^{-1}$	20 $\mu\text{g mL}^{-1}$	30 $\mu\text{g mL}^{-1}$	40 $\mu\text{g mL}^{-1}$	50 $\mu\text{g mL}^{-1}$
	K_f	K_f	K_f	K_f	K_f
S-1	0.988	1.980	3.468	6.220	7.930
S-2	0.019	0.025	0.178	0.231	0.385
S-3	0.237	0.838	0.943	1.790	2.933

The soil organic carbon- water distribution coefficient (K_{doc}) was found to be helpful in estimation of adsorption properties of the herbicide in soil. The K_{doc} values for metribuzin in soils were 74.64(S-1), 35.48(S-2), 121.70(S-3). The highest and the lowest K_{doc} values were observed in soils with low to the organic carbon content. These K_{doc} values are in the range of K_{doc} coefficients for metribuzin described by Johnson (2001) [20]. The K_{oc} values of metribuzin computed by Bakhsh *et al.* (2004) [21] and Kah and Brown (2007) [22] were 109 and 66 for different soils. These values were considered to be low, indicating a high risk of mobility of metribuzin.

Adsorption-desorption

Desorption studies were carried out in these soils over a period of five consecutive days by successive withdrawal and dilution of the supernatant and re-establishment of equilibrium of soils on which the metribuzin was previously adsorbed. Complete desorption pattern for the three soils tested at different concentrations *i.e.* 10, 20, 30, 40 and 50 $\mu\text{g mL}^{-1}$ are presented in the **Figures 4-6**.



Figures 4-6 Adsorption isotherms of metribuzin on selected soil samples in different days (S-1), (S-2) and (S-3)

The adsorption data and the isotherms showed consistent hysteresis during desorption. The percent desorption varied between 23.93 to 50.18 % in S-1; 78.34 to 51.81 % in S-2 and 66.34 to 37.42% in S-3 sample. At 10 $\mu\text{g mL}^{-1}$ concentration, desorption varied between 50.18 to 78.34 %. The desorption in the tested soils at different initial concentration varied from 38.71 % to 70.82 % at 20 $\mu\text{g mL}^{-1}$; 33.68 to 58.13 % at 30 $\mu\text{g mL}^{-1}$; 27.18 to 57.79 % at 40

$\mu\text{g mL}^{-1}$ and 23.93 to 51.81 % at $50 \mu\text{g mL}^{-1}$ concentrations. Desorption data indicated that hysteresis was highest in S-1 and lowest in S-2 and intermediate in S-3, which specified that, the desorption in the soil is strongly influenced by the clay and organic matter content. Cumulative desorption percentages calculated in the present study are in agreement with the findings of Ouzna *et al.* (2013) [9] where in metribuzin desorption isotherms showed a hysteresis and only 30 to 40 % of the initially adsorbed metribuzin was desorbed.

The variations in percent desorbed metribuzin among different soils is due to heterogeneity involved in different soils, and it widely varied in type and energy of bonding. In general, the amount of herbicide desorbed during first washing was higher and the amount progressively decreased with each subsequent washings [9]. The per cent cumulative desorption revealed that the adsorption of these herbicides is more strong indicating that the soil organic matter and clay content plays an important role in the adsorption – desorption. At low level of initial concentrations of the adsorbed herbicide, the desorption isotherms were close to adsorption isotherms there by indicating an increase in the degree of reversibility in adsorption – desorption. 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 of atrazine and isoproturon [23].

In the present study, one of the possible causes of the higher hysteresis in S-1 sample with higher clay content can be linked to the high or low clay content and the soil/solution ratio relatively high (1/2) which would favor the diffusion into the clay microporosity but decrease the reverse diffusion to the solution during the desorption steps [9].

Dissipation was inversely proportional to the amount initially adsorbed. Thus for all soils, the cumulative percent adsorbed at the end of five days decreased with increase in initial concentration from 10 to $50 \mu\text{g mL}^{-1}$. The percent desorbed for each initial concentration of metribuzin was found to decrease with the increase in clay content and organic carbon. The desorption process exhibited pronounced hysteresis in case of all the three soils tested at higher concentrations and the hysteresis decreased with decrease in the initial concentration. Desorption data was analyzed by Freundlich equations and K_f values obtained are presented in the Table 3. It is evident from the data that, K_f values increased with increase in initial concentration for all the soils. No sequence was recorded in case of ‘n’ values hence the values are not presented. The desorption K_f values varied between 0.988 ($10 \mu\text{g mL}^{-1}$) to 7.930 ($50 \mu\text{g mL}^{-1}$) in S-1; 0.019 ($10 \mu\text{g mL}^{-1}$) to 0.385 ($50 \mu\text{g mL}^{-1}$) in S-2 and 0.237 ($10 \mu\text{g mL}^{-1}$) to 2.930 ($50 \mu\text{g mL}^{-1}$) in S-3.

This kind of adsorption and desorption behaviour shown by isotherms depicted that metribuzin is strongly retained by the soil. This adsorption is not completely reversible, the desorption isotherms showing hysteresis. According to some authors, observed hysteresis in case of metribuzin can have several origins such as capture of pesticide molecules in the micro-porosity of the soil constituents or irreversible chemical bond formation [24]. In the studies conducted by Rigi *et al.* (2015) [10] on desorption of metribuzin similar results indicating the higher hysteresis effect in the soils with higher adsorption capacity and these soils were most effective in retaining metribuzin, presumably because of the highest organic carbon content.

Conclusion

Adsorption isotherms obtained for soil samples for metribuzin exhibited parabolic nature with a S-shaped character indicating a competition of water molecules to clay surface as compared to herbicide, respectively. Higher metribuzin adsorption and larger Freundlich K values was observed in soils with higher clay content and organic carbon content. Higher K_d and K_{doc} values were noticed in soils with higher clay content and organic carbon content indicating the stronger affinity of metribuzin for the organic matter in the soil. Desorption isotherms of soil adsorbed metribuzin showed hysteresis, which was more when the desorption was carried out from higher levels of initial concentrations of herbicide solution. Hysteresis was more pronounced at higher initial concentrations of herbicides.

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