

## Adsorption and Desorption Behavior of Herbicide Metribuzin in Different Soils of Iran

M. R. Rigi<sup>1</sup>, M. Farahbakhsh<sup>1\*</sup>, and K. Rezaei<sup>2</sup>

### ABSTRACT

In this study, the batch equilibrium method was used to conduct metribuzin adsorption/desorption experiments with eight soils from different regions of Iran. The results indicated that the organic carbon (OC) content, clay content, cation exchange capacity (CEC), and pH had a combined effect on the metribuzin adsorption on soil. Under the experimental conditions, the adsorption amount of metribuzin on soils was positively correlated with the content of soil organic carbon. Freundlich adsorption isotherm provided the best fit for all adsorption and desorption data. The values of  $K_{f-ads}$ , Freundlich adsorption capacity, ranged from 0.16 to 2.53 L kg<sup>-1</sup>. Soil organic carbon content and pH were the main factors influencing adsorption. Adsorption was positively correlated with OC and negatively correlated with pH. Metribuzin desorption showed that almost all of the adsorbed metribuzin was desorbed in all soils, except soil 1 and 8. However, adsorption was not completely reversible.

**Keywords:** Hysteresis, Metribuzin, Soil, Soil organic carbon, Soil pH.

### INTRODUCTION

The increasing worldwide need for food demands a higher agricultural productivity, which can partly be achieved through the use of pesticides. Unfortunately, pesticides contaminate the environment through intensive or inappropriate use (Commission of the European Communities, 1991; Dhawan *et al.*, 2009). The negative impact of the use of pesticides on human health and on the environment has attracted much attention (Brown *et al.*, 2003; Hendawi *et al.*, 2013; Liaghat and Prasher, 2003). Quantifying the fate of applied herbicides in the soil is essential for minimizing their mobility in the soil environment (Selim and Naqin, 2011).

The herbicide Metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-

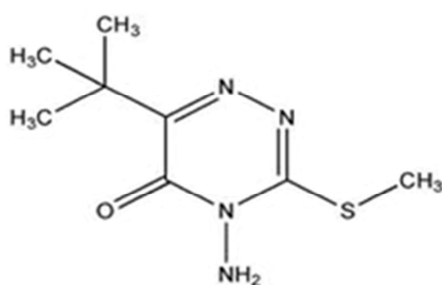
5(4H)-one ], a triazine, is widely used as a selective herbicides for pre and postemergence control of annual grasses (Papadakis and Mourkidou, 2002; Worthing, 1987) and numerous broadleaf weeds in the field and vegetable crops, turf grass, and on fallow lands by inhibiting photosynthesis of susceptible plant species (WSSA, 1994). Metribuzin is a white crystalline solid compound with a molar mass of 214.3 g mol<sup>-1</sup> and solubility of about 1.22 g L<sup>-1</sup> in water. It is highly soluble in most organic solvents including acetone (820 g L<sup>-1</sup>) and methanol (450 g L<sup>-1</sup>). Metribuzin is a heterocyclic, basic organic molecule and its molecular formulation is C<sub>8</sub>H<sub>14</sub>N<sub>4</sub>OS (Figure 1) (Kidd and James, 1991).

The adsorption–desorption behavior of a soil-applied herbicide is one of the most important factors governing its

<sup>1</sup> Department of Soil Science, University College of Agriculture and Natural Resources, University of Tehran, Karaj, 31587-77871, Islamic Republic of Iran.

\* Corresponding author; e-mail: mfbakhsh@ut.ac.ir

<sup>2</sup> Department of Food Science, University College of Agriculture and Natural Resources, University of Tehran, Karaj, 31587-77871, Islamic Republic of Iran.



**Figure 1.** The chemical structure of metribuzin.

environmental impacts such as degradation, transition, and leaching (Pusino, 2004). Soil is a heterogeneous mixture of several components, many of which are organic and inorganic compounds of varying compositions and surface activities, and may thereby considerably affect the herbicide behaviors. Various soil characteristics such as organic carbon content, clay content, pH, and CEC have been determined to affect the adsorption–desorption of herbicides (Lin *et al.*, 1997; Morrica *et al.*, 2000; Pusino, 2004).

Based on the U.S Environmental Protection Agency health advisory report, metribuzin level for drinking water is  $175 \mu\text{g L}^{-1}$ . Metribuzin concentrations in ground water were reported in the range of  $0.60\text{--}6.80 \mu\text{g L}^{-1}$  (Goodrich *et al.*, 1991). Triazine herbicides are weakly basic and can be adsorbed to both soil organic carbon and clay minerals (Goss, 1992; Weber, 1994)

and as the soil pH decreases, the adsorption increases slightly (Landlie *et al.*, 1976). The extent to which metribuzin leaches to ground water is an inverse function of organic matter content of soil. Its half-life in soil ranges between 2.5 and four months (Sharom and Stephenson, 1976).

No data has been published on the adsorption–desorption of metribuzin in Iranian soil. The objectives of this research were: (1) to study the detailed adsorption isotherms and desorption characteristics of metribuzin in eight types of soils with various physical and chemical properties, (2) to quantify metribuzin desorption hysteresis, and (3) to investigate the influence of soil properties on its adsorption–desorption.

## MATERIALS AND METHODS

### Soil Samples

The eight soil samples used in this study were collected from agricultural fields and contained no detectable amount of metribuzin residues. Samples taken from the plow layer (0-20 cm), were air dried at room temperature, mixed thoroughly, and sieved through 2 mm mesh. Some physical and chemical properties of the soils were determined, which are summarized in Table 1. Soil pH was measured in 1:2.5 soil-water suspension with a glass pH electrode, the soil organic carbon was measured by

**Table 1.** The physical and chemical properties of the tested soils.

Soil No.	Textural Class	pH	Organic Carbon	Clay %	Sand	Silt	CEC <sup>a</sup>
1	Loam	7.73	2.33	25.4	40.96	33.64	23.15
2	Loam	8.01	0.475	23.4	38.96	37.64	22.23
3	Clay Loam	7.82	0.62	37.4	36.96	25.64	30.35
4	Clay Loam	7.64	1.38	29.4	32.96	37.64	25.36
5	Silty Clay	7.78	0.76	45.4	14.96	39.64	34.97
6	Clay Loam	7.96	0.475	31.4	36.96	31.64	17.48
7	Loam	7.6	0.475	13.4	50.96	35.64	12.77
8	Sandy Loam	7.97	0.62	19.4	58.96	21.64	20.62

<sup>a</sup> cation exchange capacity

oxidation method with  $K_2Cr_2O_7-H_2SO_4$ . The CEC was determined by the ammonium acetate method, soil particle fractions were determined by the hydrometer method (Gee and Bauder, 1988).

### Herbicide and Chemicals

Analytical grade metribuzin with purity of 99% was used for the present study. The organic reagents used included acetonitrile, ethyl acetate, calcium chloride, and sodium sulfate, all of analytical grade. Standard stock solution of metribuzin ( $1,000 \text{ mg L}^{-1}$ ) was prepared in acetonitrile and stored in the dark at  $4^\circ\text{C}$ . Working standard solutions were prepared by appropriate dilutions in  $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$  solution ( $0.01\% \text{ NaN}_3$ ).

### Adsorption/Desorption Experiments

Adsorption experiments were carried out using the batch equilibrium technique. Five gram of air-dried soil was placed in 50 mL Teflon centrifuge tubes with screw caps and equilibrated with 25 mL of  $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$  solution ( $0.01\% \text{ NaN}_3$ ) containing 6 different concentrations of metribuzin (0.07, 0.1, 0.3, 0.5, 0.7,  $1 \text{ mg L}^{-1}$ ). One series of tubes without soil was also monitored as the control to determine the effects of metribuzin adsorption onto the tubes and the following possible degradation of metribuzin during the process. The amount of metribuzin adsorption to centrifuge tubes was negligible ( $< 1\%$ ). Thus, the reduced herbicide in solution was considered to be responsible only for soil adsorption. Then, soil suspensions were shaken on a reciprocating shaker for 24 hours at  $25\pm 1^\circ\text{C}$  in dark. Preliminary experiments indicated that 24 hours shaking was sufficient to reach the apparent equilibrium (result not shown). Subsequently, the suspensions were centrifuged at 4,500 rpm for 15 minutes. After extraction of the analyte from the solution, it was analyzed by gas chromatography. The amount of metribuzin

adsorbed was calculated from the difference between the initial and final concentration in solution. All experiments were conducted in duplicate.

Desorption experiments began immediately after the adsorption experiment. Supernatants with the volume of 5 mL were withdrawn from the adsorption treatments with 0.5, 0.7, and  $1 \text{ mg L}^{-1}$ , respectively, and were replaced with the same volume of metribuzin-free  $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$  solution and, then, samples were re-equilibrated on a reciprocating shaker for 24 hours at  $25\pm 1^\circ\text{C}$ . After that, the samples were centrifuged for 15 min at 4,500 rpm. These steps were repeated four times consecutively. Subsequent analyses were conducted as described above. The concentration of metribuzin in solutions was determined, and the amount of desorbed metribuzin by the soil after each adsorption step was calculated. Thus, each level of dilution, provided one point to the desorption isotherms.

### Effect of pH on Adsorption

The adsorption experiments were conducted at different pH values of  $0.01 \text{ M CaCl}_2$  solutions by addition of HCl and NaOH. The pH of solutions were adjusted to 4.5, 6.5 and 8.5 respectively. The initial concentrations of metribuzin were 0.07, 0.1, 0.3, 0.5, 0.7, and  $1 \text{ mg L}^{-1}$ . Then, the test was carried out in the same way as the batch equilibration experiments described above. In this study, three different types of soils were used to determine pH effect on metribuzin adsorption in soils.

### Metribuzin Extraction and Analysis

Metribuzin residue from solution was extracted as below: A 1-ml aliquot was sampled from the supernatant and 2 mL of ethyl acetate was added and shaken for 1 minute. After shaking, the samples were left for 1 minute and 1 g of anhydrous sodium



sulfate was added to each tube to remove any trace of moisture from the ethyl acetate fraction (Majumdar and Singh, 2007). The upper ethyl acetate layer was collected to determine metribuzin concentration and stored at 4°C prior to analysis by gas chromatography equipped with electron capture detector (GC-ECD). Metribuzin concentrations in the ethyl acetate fraction were quantified by an Agilent, 7890A GC equipped with <sup>63</sup>Ni electron capture detectors (ECD) and fitted with HP-5 column [30 m long×0.32 mm (id)×0.25 μm (film thickness)]. The gas chromatograph operating conditions were: initial oven temperature 120°C, oven temperature 120 to 270°C at 20 °C min<sup>-1</sup> with a final holding time of 0.5 minutes, detector temperature, 300 °C, injector temperature 300°C and carrier gas (N<sub>2</sub>) flow rate (99.99% purity) 5 mL min<sup>-1</sup>. Under these conditions, retention time of metribuzin was 6.248 min. Recovery of metribuzin from samples was more than 92.5%. The concentration of analyte was quantified using external standards in the range of 0.01-5 mg L<sup>-1</sup>.

### Data Analysis

Amounts of adsorbed metribuzin were determined by the mass balance equation, expressed as Equation (1):

$$q = \frac{v(c_i - c)}{m} \quad (1)$$

Where,  $q$  is the specific adsorbed amount of solute (mg kg<sup>-1</sup>),  $V$  is the volume of the equilibrium solution (25 mL),  $C_i$  and  $C$  represent the initial concentration and the remaining solution concentration of metribuzin (mg L<sup>-1</sup>), respectively, and  $m$  is the mass of the air-dried soil (g). The two most widely used linearized form of the equations, Freundlich and Langmuir, were employed to describe adsorption and desorption isotherms and are defined as Equations (2) and (3), respectively:

$$\text{Log}q = \text{Log}Kf + \frac{1}{nf} \text{Log}C \quad (2)$$

$$\frac{C}{q} = \frac{1}{kb} + \frac{1}{b}C \quad (3)$$

Where,  $q$  is the metribuzin concentration on the soil after adsorption/desorption (mg kg<sup>-1</sup>),  $C$  is the metribuzin equilibrium concentration in solution (mg L<sup>-1</sup>), and  $K_f$  and  $n$  are the adsorption coefficients characterizing the adsorption-desorption capacity and the Freundlich equation exponent related to adsorption intensity that is used as an indicator of the adsorption isotherm nonlinearity, respectively, and  $b$  is the maximum adsorption capacity;  $K$  is the Langmuir constant, which is indicative of relative adsorption energy.

The OC-normalized constant ( $K_{oc}$ ) was calculated for adsorption as Equation (4):

$$K_{oc} = \frac{kd}{\%oc} \times 100 \quad (4)$$

Where,  $K_d$  as the distribution coefficient, was calculated by the equation  $K_d = q/C$ ,  $q$  and  $C$  are the same as above; % OC is the percentage of organic carbon of soil (Hamaker and Tompson, 1972). The hysteresis coefficient,  $H$ , for the adsorption and desorption isotherms was calculated according to Equation (5):

$$H = \frac{nd}{n} \quad (5)$$

Where,  $n$  and  $n_d$  are the Freundlich constants obtained for the adsorption and desorption isotherms, respectively (Barriuso *et al.*, 1994). Relationships between soil properties and adsorption coefficients were tested by Pearson correlation. The statistical analysis and model development were performed using the software SPSS 16.0 for Windows.

## RESULTS AND DISCUSSION

### Soil Characteristics

As shown in Table 1, the soil characteristics varied widely. The organic carbon content varied from 0.475 to 2.33%. Soil pH ranged from 7.60 to 8.01, and clay

content varied from 13.4 to 45.4%. The CEC ranged from 12.77 to 34.97 cmol (+) kg<sup>-1</sup>. Among soil properties, the organic carbon content was positively correlated with clay content and CEC, and was negatively correlated with pH and sand content. The clay content was positively related to the CEC, but was negatively related to sand content. The sand content was negatively correlated with silt and CEC (Table 2).

### Adsorption Isotherm

The simulation parameters of Freundlich and Langmuir Models are presented in Table 3. The results showed that the coefficients of determination ( $r^2$ ) and Langmuir constants

of most of the soils were significant, but for Freundlich equations, both coefficients of determination ( $r^2$ ) and the constants ( $K$ ;  $n$ ) were significant. The results indicated that the isotherms were well described by the Freundlich equation. Vryzas *et al.* (2007) described the same result for metolachlor, atrazine, and three conversion products of atrazine. The adsorption of metribuzin by soils increased with solution concentration (Figure 2), suggesting that adsorption sites were not saturated at the concentrations used in this study (except for soils 1 and 7). The adsorption of metribuzin in the different soils studied increased in the order: soil 1 > soil 8 > soil 4 > soil 5 > soil 3 > soil 6 > soil 2 ≈ soil 7. Therefore, it can be concluded that soils number 1, 8, and 4 had high adsorption

**Table 2.** Correlation coefficients between soil properties for the 8 soils studied (N= 8).

	Organic Carbon	pH	Clay	Sand	Silt	CEC <sup>a</sup>
Organic Carbon	1					
pH	-0.421	1				
Clay	0.022	0.074	1			
Sand	-0.101	0.138	-0.877**	1		
Silt	0.170	-0.402	0.188	-0.637*	1	
CEC	0.166	0.010	0.874**	-0.750*	0.131	1

<sup>a</sup> Cation Exchange Capacity.

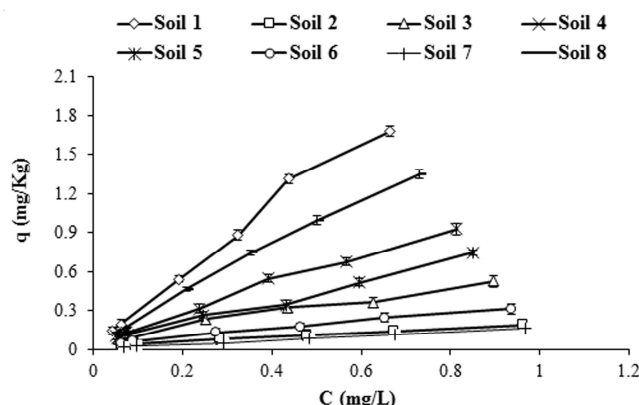
\*\* Correlation is significant at 0.01 probability level, \* Correlation is significant at 0.05 probability level.

**Table 3.** Adsorption constants and coefficient of determination ( $r^2$ ) of metribuzin on the eight soils based on the Freundlich and Langmuir equations.

Soil	Freundlich			Langmuir			
	$K_{f-ads}$ <sup>a</sup> (L kg <sup>-1</sup> )	$1/n_{f-ads}$ <sup>a</sup>	$r^2$	$K_{OC}$ <sup>b</sup> (L kg <sup>-1</sup> )	$K^c$	$b^d$	$r^2$
1	2.53**	0.908**	0.997**	108.584	0.445**	7.407*	0.673*
2	0.18**	0.609**	0.989**	37.895	1.721**	0.274**	0.861**
3	0.57**	0.727**	0.991**	91.935	1.391**	0.874**	0.919**
4	1.08**	0.804**	0.997**	78.261	0.853**	2.155**	0.84**
5	0.75**	0.741**	0.989**	98.684	0.351**	4.115*	0.685*
6	0.32**	0.678**	0.997**	67.368	1.452**	0.504**	0.895**
7	0.16**	0.895**	0.982**	33.684	1.497**	0.667	0.817
8	1.81**	0.873**	0.999**	291.935	0.597**	4.348**	0.895**

<sup>a</sup>  $K_{f-ads}$  is the Freundlich empirical constant indicative of the adsorption capacity;  $n_{f-ads}$  is the Freundlich empirical constant indicative of the adsorption intensity; <sup>b</sup>  $K_{OC}$  is the organic carbon-normalized constant, <sup>c</sup>  $K$  is the Langmuir constant, which is indicative of relative adsorption energy, <sup>d</sup>  $b$  is the maximum adsorption capacity of Langmuir model.

\*\* Correlation is significant at 0.01 probability level, \* Correlation is significant at 0.05 probability level.



**Figure 2.** Adsorption isotherms of metribuzin on eight soils.  $q$  is the amount of metribuzin adsorbed per unit weight of soil and  $C$  is the equilibrium metribuzin concentration.

capacity for metribuzin; while soils number 2, 6, and 7 had low adsorption capacity. The highest adsorption capacity ( $K_f= 2.53$ ) of soil 1 was about 16-fold of the lowest adsorption capacity ( $K_f= 0.16$ ) of soil 7. The calculated  $K_f$  by Johnson and Pepperman (1995) and Lagat *et al.* (2011) are in the range of  $K_f$  coefficients for metribuzin in the present study.

Simple correlation coefficients between soil properties and adsorption parameters ( $K_f$ ;  $n$ ) of metribuzin are summarized in Table 4. There was a significant positive relationship between the  $K_f$  and the OC content ( $r= 0.809$ ,  $P< 0.01$ ), while the relationship between the  $n$  value and the OC content ( $r= 0.500$ ) was negative. It is difficult to understand the nature of the relationship between OC and  $K_f$  only by simple correlation analysis. Soil organic carbon has a main role in adsorption of pesticides (Arias-Estévez *et al.*, 2008). The adsorption of s-triazines on organic carbon is governed by H bonds and proton transfer

between s-triazines and acidic groups of humic substances (Barriuso *et al.*, 1997; García-Valcárcel and Tadeo, 1999). The  $K_{oc}$  values for the metribuzin in eight soils varied from 33.684 to 291.935 ( $L\ kg^{-1}$ ) (Table 3). These values are in the range of  $K_{oc}$  coefficients for metribuzin described by Johnson (2001). The relatively high  $K_{oc}$  values determined in this study for soils 8, 1, and 5 suggest the contribution of mineral constituents as well as soil organic carbon. Adsorption studies of s-triazines have indicated a stronger interaction between s-triazine and organic carbon than between s-triazine and clay. As data have shown, the metribuzin adsorption was stronger in soil with higher organic carbon (Table 1; Figure 2).

### pH Effect on Metribuzin Adsorption

Soil pH has important role in controlling the dissociation or protonation process of

**Table 4.** The bivariate correlation between  $K_f$ ,  $n$  and soil properties ( $N= 8$ ).<sup>a</sup>

	Organic Carbon	pH	Clay	Sand	Silt	CEC <sup>b</sup>
$K_f$	0.809** <sup>c</sup>	-0.099	-0.089	0.219	-0.305	0.134
$n$	-0.500	0.640* <sup>d</sup>	0.372	-0.408	0.239	0.212

<sup>a</sup>  $K_f$  is the Freundlich empirical constant indicative of the adsorption capacity;  $n$  is the Freundlich empirical constant indicative of the adsorption intensity, <sup>b</sup> Cation Exchange Capacity

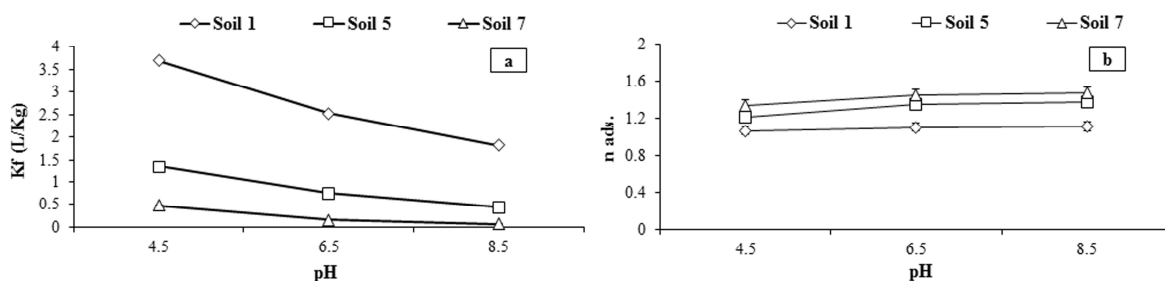
\*\* Correlation is significant at 0.01 probability level, \* Correlation is significant at 0.05 probability level.

both the herbicide and the adsorbent surface; therefore, the metribuzin adsorption on the three tested soils was affected by changing pH of the solution. The results showed that the  $K_f$  values and  $n$  for metribuzin were changed independent of pH values in the three selected soils (Figure 3). The  $K_f$  coefficient of metribuzin adsorption on soils was rather high at low pH values and decreased with the increasing pH values of the suspension (Figure 3-a). As shown in Figure 3b, in adsorption of metribuzin in soils, the  $n$ -parameter varied from low values at pH 4.5 to higher values at pH 8.5, showing high affinity at a low pH value, whereas low affinity at a high pH value. This indicates that the availability of the adsorption sites to metribuzin molecules is reduced as the pH value increase. The increase of solution pH decreased the fraction of positively charged metribuzin species; therefore, metribuzin adsorption were reduced on the negatively charged organic matter surfaces. Gao *et al.* (1998) reported the same result for triazine herbicides and also stated that the maximum adsorptions of *s*-triazine herbicides were achieved when the solution pH values were near their pK values of 1.7–2.6. The pH could play an important role if pesticides and herbicides exist in cationic, anionic, or nonionic forms. Moreover, Pang *et al.* (2007) stated that the low water solubility of pesticide at low pH could contribute to the high adsorption level because the retention of a pesticide onto organic surface is often

inversely correlated with its water solubility.

### Desorption Characteristics

Table 5 shows desorption of metribuzin in soils at different concentrations. The  $1/n_{f-des}$  values (Table 5) were higher than the  $1/n_{f-ads}$  values (Table 3). At the same time, desorption hysteresis coefficient,  $H$ , was found to be close to 1 in most of the soils ( $H$  ranged from 0.631 to 0.954). Generally, a value of  $H$  close to 1 means that desorption proceeds as quickly as adsorption does; therefore, hysteresis is absent. On the other hand, a value of  $H < 1$  indicates that the rate of desorption is lower than that of adsorption, thus, hysteresis takes place (Pusino *et al.*, 2004). Except for soil 1, metribuzin desorption from all other soils were not hysteretic (Table 5), suggesting that a significant amount of the metribuzin adsorbed was easily desorbed and the metribuzin adsorption by soil was reversible. In this study, it was shown, that the hysteresis coefficient values of all soils decreased with increasing initial metribuzin concentrations. This result was in contrast to some studies, which suggested that more molecules were taken up by low-energy binding sites at high solute concentration and, therefore, could be readily desorbed (Gao *et al.* 1998; Gunasekara and Xing, 2003). Majumdar and Singh (2007) found a similar result and suggested that metribuzin was very poorly retained in the natural soil and all of the adsorbed metribuzin was



**Figure 3.** Effect of pH values on adsorption of metribuzin in soils.  $K_f$  and  $n_{ads}$  are the Freundlich empirical constants indicative of capacity and intensity of adsorption, respectively.

**Table 5.** Freundlich parameters, coefficients of determination ( $r^2$ ), and hysteresis coefficients (H) for desorption of metribuzin in five soils.<sup>a</sup>

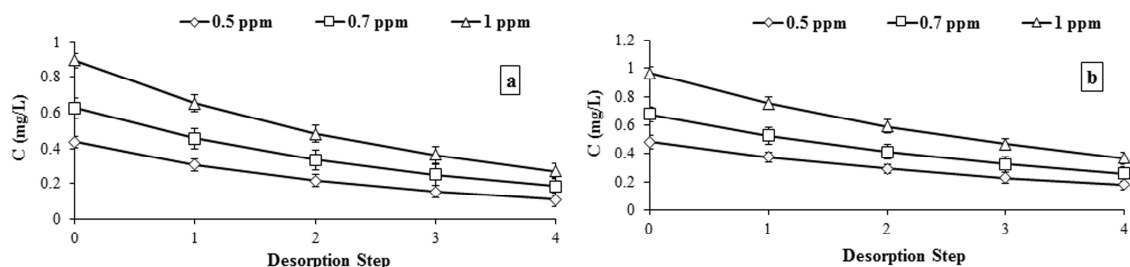
Soil No.	Initial Concentration (mg L <sup>-1</sup> )	$K_{f-des}^a$	$1/n_{f-des}^b$	$r^2$	H	$H_a^c$
1	0.5	$4.55 \pm 0.002^d$	$1.220 \pm 0.009$	0.989	0.715	0.631
	0.7	$4.26 \pm 0.005$	$1.289 \pm 0.008$	0.997	0.677	
	1	$3.53 \pm 0.007$	$1.750 \pm 0.002$	0.981	0.499	
3	0.5	$0.63 \pm 0.007$	$0.971 \pm 0.005$	0.993	0.922	0.894
	0.7	$0.39 \pm 0.005$	$0.994 \pm 0.001$	0.996	0.901	
	1	$0.46 \pm 0.002$	$1.042 \pm 0.008$	0.998	0.859	
5	0.5	$0.68 \pm 0.005$	$0.839 \pm 0.005$	0.993	0.883	0.844
	0.7	$0.78 \pm 0.002$	$0.877 \pm 0.001$	0.993	0.845	
	1	$0.85 \pm 0.011$	$0.923 \pm 0.001$	0.998	0.803	
7	0.5	$0.15 \pm 0.004$	$0.729 \pm 0.009$	0.988	0.997	0.954
	0.7	$0.19 \pm 0.008$	$0.751 \pm 0.009$	0.992	0.968	
	1	$0.10 \pm 0.005$	$0.811 \pm 0.005$	0.991	0.896	
8	0.5	$2.45 \pm 0.002$	$1.119 \pm 0.001$	0.995	0.781	0.736
	0.7	$2.68 \pm 0.007$	$1.184 \pm 0.005$	0.994	0.737	
	1	$2.31 \pm 0.005$	$1.262 \pm 0.004$	0.995	0.692	

<sup>a</sup>  $K_{f-des}$  is the Freundlich empirical constant indicative of the desorption capacity; <sup>b</sup>  $n_{f-des}$  is the Freundlich empirical constant indicative of the desorption intensity; <sup>c</sup> Average values of H; <sup>d</sup> Mean  $\pm$  standard deviation.

desorbed during the desorption step. Also, the amount and strength of metribuzin adsorption increased by adding organic carbon to soils. The correlation between desorption hysteresis (averaged H values) and soil organic carbon was determined ( $r = -0.817$ ,  $P = 0.046$ ). The highest hysteresis effect (lowest H) was observed in Soil 1, which had the highest adsorption capacity (Table 5) and was the most effective in retaining metribuzin, presumably because of the highest organic carbon content. Harper (1988) found that the magnitude of metribuzin adsorption on surface soil was positively correlated to soil OC and

clay content; however, adsorption was not completely reversible.

The results of metribuzin desorption versus time are shown in Figures 4-a and 4-b (for soils 3 and 7, respectively): a decrease in metribuzin concentration in solution was observed after each successive desorption step. The relationship between metribuzin concentration in solution and desorption time was described using an exponential equation. During four desorption steps, the differences of metribuzin concentration in solution among the initial concentration treatments of 0.5, 0.7 and 1 mg L<sup>-1</sup>, in all soils were significant ( $P <$



**Figure 4.** Metribuzin concentration in solution with time during desorption from soil 3 (a) and soil 7 (b) equilibrated with three initial metribuzin concentrations. The concentrations of metribuzin at day 0 of desorption time meant the metribuzin concentrations at 24 hours of adsorption time in the adsorption experiment.



0.01). As shown in Figure 4, desorption pattern of metribuzin was biphasic, a slow desorption following an initial fast phase.

### CONCLUSIONS

Batch experiment has shown that different kinds of soils have different adsorption capacities for metribuzin. The adsorption capacity of metribuzin, which was positively correlated with soil organic carbon content, was the highest in soil 1, while that of soils 2 and 7 were the lowest. The pH of the solution controlled metribuzin adsorption in the studied soils. It is concluded that the availability of the adsorption sites to metribuzin molecules is reduced as the pH increases. The main reason for the high extent of metribuzin adsorption measured at low pH may be due to the lack of charge and higher lipophilicity of the neutral molecular species within the herbicide. The metribuzin desorption in almost all of the soils was not hysteretic, therefore, a significant amount of the metribuzin adsorbed was easily desorbed in four steps. However, adsorption was not completely reversible.

### ACKNOWLEDGEMENTS

This research was financially supported by the University of Tehran. We thank Institute of Plant Protection Research, Iran, for providing metribuzin standard. The authors have declared no conflict of interest.

### REFERENCES

1. Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J. and García-Río, L. 2008. The Mobility and Degradation of Pesticides in Soils and the Pollution of Groundwater Resources. *Agric. Ecosyst. Environ.*, **123**: 247–260.
2. Barriuso, E., Houot, S. and Serra-Wittling, C. 1997. Influence of Compost Addition to Soil on the Behavior of Herbicides. *Pestic. Sci.*, **49**: 65–75.
3. Barriuso, E., Laird, D. A., Koskinen, W. C. and Dowdy, R. H. 1994. Atrazine Desorption From Smectites. *Soil Sci. Soc. Am. J.*, **58**: 1632–1638.
4. Brown, C. D., Hart, A., Lewis, K. A. and Dubus, I. G. 2003. p-EMA (I): Simulating The Environmental Fate of Pesticides for a Farm-Level Risk Assessment System. *Agronomie*, **23**: 67–74.
5. Commission of the European Communities. 1991. Directive 91/414/EEC, Directorate General for Agriculture, DG VI B II-1. Brussels, Belgium.
6. Dhawan, A. K., Singh, S. and Kumar, S. 2009. Integrated Pest Management (IPM) Helps Reduce Pesticide Load in Cotton. *J. Agr. Sci. Tech.*, **11**: 599-611.
7. Gao, J. P., Maguhn, J., Spitzauer, P. and Kettrup, A. 1998. Sorption of Pesticides in the Sediment of the Teufelsweiher Pond (Southern Germany) I. Equilibrium Assessments, Effect of Organic Carbon Content and pH. *Water Res.*, **32**: 1662–1672.
8. Gao, J. P., Maguhn, J., Spitzauer, P. and Kettrup, A. 1998. Sorption of Pesticides in the Sediment of the Teufelsweiher Pond (Southern Germany) II. Competitive Adsorption, Desorption of Aged Residues and Effect of Dissolved Organic Carbon. *Water Res.*, **32**: 2089–2094.
9. García-Valcárcel, A. and Tadeo, J. 1999. Influence of Soil Moisture on Sorption and Degradation of Hexazinone and Simazine in Soil. *J. Agr. Food Chem.*, **47**: 3895–3900.
10. Gee, G. W. and Bauder, J. W. 1988. Particle-size Analysis. Part 1. In: *Methods of Soil Analysis*, (Ed.): Klute, A.. American Society of Agronomy and Soil Science, Madison, WI, PP. 383–441.
11. Goodrich, J. A., Benjamin, W. L. J. and Robert, M. C. 1991. Drinking Water from Agriculturally Contaminated Groundwater. *J. Environ. Qual.*, **20**: 707-717.
12. Goss, D. W. 1992. Screening Procedures for Soils and Pesticides for Potential Water Quality Impact. *Weed Technol.*, **6**: 701-709.
13. Gunasekara, A. S. and Xing, B. 2003. Sorption and Desorption of Naphthalene by Soil Organic Matter Importance of Aromatic and Aliphatic Components. *J. Environ. Qual.*, **32**: 240–246.



14. Hamaker, J. W. and Tompson, J. M. 1972. *Adsorption of Organic Chemicals in the Soil Environment*. Marcel Dekker, New York, PP. 49-144.
15. Harper, S. S. 1988. Sorption of Metribuzin in the Surface and Surface Soils of the Mississippi Delta Region. *Weed Sci.*, **36**: 84-89.
16. Hendawi, M. Y., Romeh, A. A. and Mekky, T. M. 2013. Effect of Food Processing on Residue of Imidacloprid in Strawberry Fruits. *J. Agr. Sci. Tech.*, **15**: 951-959.
17. Johnson, A. B. 2001. Adsorption and Degradation of Metolachlor and Metribuzin in a No-Till System under Three Winter Crop Covers. *Soil Sediment Contam.*, **10**: 525-537.
18. Johnson, R. M., and Pepperman, A. B. 1995. Analysis of Metribuzin and Associated Metabolites in Soil and Water Samples by Solid Phase Extraction and Reversed Phase Thin Layer Chromatography. *J. Liq. Chromatogr.*, **18**: 739-753.
19. Kidd, H. and James, D. R. 1991. *The Agrochemicals Handbook*. 3<sup>rd</sup> Edition. Royal Society of Chemistry Information Services, Cambridge, UK.
20. Lagat, S. C., Lalah, J. O., Kowenje, C. O. and Geteng, Z. M. 2011. Metribuzin Mobility in Soil Column as Affected by Environmental and Physico-Chemical Parameters in Mumias Sugarcane Zone, Kenya. *J. Agr. Biolo. Sci.*, **6**: 27-33.
21. Landlee, J. S., Maggitt, W. F. and Penner, D. 1976. Effect of pH on Microbial Degradation, Adsorption and Mobility of Metribuzin. *Weed Sci.*, **24**: 477-481.
22. Liaghat, A. and Prasher, S. O. 2003. Application of Mathematical Modeling to Determine the Size of On-Site Grass Filters for Reducing Farm Pesticide Pollution. *J. Agric. Sci. Technol.*, **5**: 125-134.
23. Lin, K. H., Yen, J. H. and Wang, Y. S. 1997. Accumulation and Elimination Kinetics of Herbicides Butachlor, Thiobencarb and Chlomethoxyfen by *Aristichthys Nobilis*. *Pestic. Sci.*, **49**: 178-184.
24. Majumdar, K. and Singh, N. 2007. Effect of Soil Amendments on Sorption and Mobility of Metribuzin in Soils. *Chemosphere*, **66**: 630-637.
25. Morrica, P., Barbato, F., Giodano, A., Serenella, S. and Francesca, U. 2000. Adsorption and Desorption of Imazosulfuron by Soil. *J. Agr. Food Chem.*, **48**: 6132-6137.
26. Pang, H. L., Yang, J. B., Huang, M. Z., Ren, Y. G. and Yin, D. L. 2007. Syntheses and Herbicidal Activity of 2-[[[(4-Methoxy-6-methylthio-2-pyrimidinyl) Amino] Carbonyl] Amino]Sulfonyl] Benzoic Acid Methyleste. *Agrichemicals*, **2**: 86-88.
27. Papadakis, E. N. and Mourkidou, E. P. 2002. Determination of Metribuzin and Major Conversion Products in Soils by Microwave-Assisted Water Extraction Followed by Liquid Chromatographic Analysis of Extracts. *J. Chromatogr. A*, **962**: 9-20.
28. Pusino, A., Pinna, V. M. and Gessa, C. 2004. Azimsulfuron Sorption-desorption on Soil. *J. Agr. Food Chem.*, **52**: 3462-3466.
29. Selim, H. M. and Naquin, B. J. 2011. Retention of Metribuzin by Sugarcane Residue: Adsorption-Desorption and Miscible Displacement Experiments. *Soil Sci.*, **176**: 520-526.
30. Sharom, M. S. and Stephenson, G. R. 1976. Behaviour and Fate of Metribuzin in Eight Ontario Soils, *Weed Sci.*, **24**: 153-160.
31. Vryzas, Z., Papadopoulou-Moukidou, E., Soulios, G. and Prodromou, K. 2007. Kinetics and Adsorption of Metolachlor and Atrazine and the Conversion Products (Deethylatrazine, Deisopropylatrazine, Hydroxyatrazine) in the Soil Profile of a River Basin. *European J. Soil Sci.*, **58**: 1186-1199.
32. Weber, J. B. 1994. Properties and Behaviour of Pesticides in Soils. In: *"Mechanism of Pesticide Movement into Groundwater"*, (Eds.): Honeycutt, R. C. and Schabacker D. J.. CRC Press, Boca Raton, FL, 1541 PP.
33. Worthing, C. R. 1987. *The Pesticide Manual: A World Compendium*. 8<sup>th</sup> Edition, The British Crop Protection Council, Thornton Heath, UK.
34. WSSA. 1994. *Herbicide Handbook of the Weed Science Society of America*. 7<sup>th</sup> Edition WF Humphrey Press, Geneva, NY.

## رفتار جذب و واجذب علف کش متری بیوزین در خاک‌های مختلف ایران

م. ر. ریگی، م. فرحبخش، و ک. رضایی

## چکیده

در این مطالعه، آزمایش‌های جذب و واجذب متری بیوزین در هشت خاک جمع آوری شده از نواحی مختلف ایران بطور تعادلی انجام گرفت. نتایج نشان داد که جذب متری بیوزین بر روی خاک‌ها تحت تاثیر مقدار کربن آلی، مقدار رس، ظرفیت تبادل کاتیونی و pH می باشد. تحت شرایط این آزمایش، مقدار جذب متری بیوزین بر روی خاک‌ها همبستگی مثبتی با مقدار کربن آلی نشان داد. داده‌های جذب و واجذب مطابقت بهتری با همدمای جذب فروندلیچ داشتند. همچنین مقادیر ضرایب جذب فروندلیچ در دامنه ۲/۵۳-۰/۱۶ لیتر در کیلوگرم قرار داشتند. عمدتاً "جذب علف کش تحت تاثیر مقدار کربن آلی و pH قرار داشت، به طوری که جذب دارای همبستگی مثبت با مقدار کربن آلی و همبستگی منفی با میزان pH داشت. نتایج آزمایش واجذب نشان داد که، تقریباً "تمامی متری بیوزین جذب شده به جز در خاک ۱ و ۸ در بقیه خاک‌ها واجذب گردیده است. لذا، جذب کاملاً "برگشت-پذیر نیست.