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Behavior of Atrazine and Malathion Pesticides in Soil: Sorption and Degradation Processes

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Abstract: The objective of this study is to evaluate the sorption characteristics of two pesticides; Atrazine and Malathion by fitting the sorption data to linear and non-linear isotherm equations and to characterize the degradation of Atrazine and Malathion under laboratory conditions. The sorption of Atrazine and Malathion in soil was studied using a batch experiment technique. Solutions with different initial Atrazine or Malathion concentrations (C_i) of 0 to 600 $\mu\text{g L}^{-1}$ in 50 $\mu\text{M L}^{-1}$ CaCl_2 were used in duplicate. Pesticide residues in solutions were extracted with acetone: hexane using ratio of 3:2 (v/v) by Microwave-Assisted Extraction technique (MAE). The sorption data were fitted in some mathematical models to obtain the sorption parameters of pesticides i.e., Linear, Freundlich, Langmuir and Exponential isotherm models. The present results indicate that the three isotherms including Freundlich, Langmuir and Exponential (proposed model) have similar accuracy in predicting the sorption process, but the proposed (Exponential) isotherm is better because it has high R^2 and less SSE. Also, Atrazine has higher affinity for binding to soil particles than Malathion. Measured degradation rate averaged about 0.0102 day^{-1} for Atrazine and 0.1053 day^{-1} for Malathion. The half-life was accounted as 68.1 and 6.6 days for Atrazine and Malathion, respectively. Therefore, Atrazine is more stable in soil than Malathion. About 78% of Atrazine was remained in soil at 25 days after application, while 8% only of Malathion was remained in soil at the same period. The findings from this study emphasize on the need for care when using persistent pesticides to control weeds in soil.

Key words: Sorption, degradation rate, Freundlich model, Langmuir model, Exponential model, sorption equilibrium constant

INTRODUCTION

Groundwater pollution from non-point sources is an important concern in many countries. In the past decade, the increase in agricultural productivity has been closely related to the use of agrochemicals such as fertilizers and pesticides. The often excessive rates of fertilizers and pesticides applied to the crops have contributed to surface and subsurface water contamination (Azevedo *et al.*, 2000). The use of agrochemicals must therefore be balanced against the need to keep the drinking water supplies safe and the increasing desire to maintain the sustainability of natural habitats for different plant and animal species.

The movement of pesticides in soils depends on the physical and chemical properties of the compound (such as soil type, organic matter, physical and chemical composition, pH, etc.) and the climatic conditions (Hornsby *et al.*, 1995). Therefore, the mobility of pesticides in soils is both of agronomic and of environmental concern. Scientists have concentrated their efforts on the elucidation of pesticides mobility in different studies on sorption,

dissipation and leaching of pesticides using soil samples in laboratory or under field conditions (Prata *et al.*, 2003).

Several studies of atrazine behavior in soils have shown a wide range in the sorption partition coefficient (K_d), which was found to be proportional to the soil organic C content (Mersie and Seybold, 1996; Moreau and Mouvet, 1997; Moorman *et al.*, 2001; Abdel-Nasser, 2005) and other soil properties (Weber *et al.*, 2004). In the database compiled by Wauchope *et al.* (1992), an average of partition coefficient of organic carbon, K_{oc} ($K_{oc} = K_d/OC\% \times 100$) of 100 mL g^{-1} and a range of K_{oc} values from 38 to 174 mL g^{-1} is listed for atrazine. In addition to the partition coefficient, which describes the equilibrium distribution of the pesticide between sorbed and dissolved states, the rate of achieving this equilibrium also determines the fate of pesticides.

Sorption of Atrazine to various components has been widely studied (Chung and Alexander, 2002; Dorado *et al.*, 2003; Alam *et al.*, 2004; Dehghani *et al.*, 2005; Correia *et al.*, 2007; Danrong *et al.*, 2009). The sorption of pesticides can be divided into a fast and a slow phase (Gamble *et al.*, 2000). The fast sorption phase includes surface processes, whereas the slow phase is

related to diffusion into and out of humic substances. The very slow diffusion process also leads to a slow release of pesticides that are sorbed in the interior of the humic matrix back into the soil solution (Prata *et al.*, 2003).

Because of sorption and degradation are the two most important processes affecting the fate and behavior of pesticides in soil, therefore the objective of this study was to evaluate the sorption characteristics of two pesticides; Atrazine (herbicide) and Malathion (insecticide) by fitting the sorption data to linear and non-linear isotherm equations.

MATERIALS AND METHODS

Soil: The soil sample used in our present study was collected from the surface layer (0-30 cm) of Kharj Province, Haradh road, Riyadh, Saudi Arabia, 24° 27' 5.8" N and 47° 40' 23.1" E and 445 m above sea level. The soil has sandy loam texture and some of its physical and chemical characteristics as determined by recommended procedures (Klute, 1986) are presented in Table 1. The pH, soil electrical conductivity and soluble cations and anions were determined in soil paste extract (Klute, 1986). The texture of soil is sandy loam and has 81.9% sand, 2.50% silt and 15.6% clay with electrical conductivity of 0.92 dS m⁻¹.

Pesticides: Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) of 99.8% purity, which is an herbicide used for selective control of grassy weeds. It has a water solubility of 33 mg L⁻¹ and half-life of 64 days (Singh *et al.*, 1990a). In the National Pesticide Survey, they found that atrazine is one of the most detected pesticides in the groundwater (Wollenhaupt and Springman, 1990). Malathion is known technically as diethyl (dimethoxy thiophosphorylthio) succinate. Malathion is a non-systemic, organophosphate insecticide. Main usage is agricultural and domestic, mainly for the control of sucking and chewing insects including mosquitoes, aphids, turf insects and many floral and vegetable crops. It has a water solubility of 145 mg L⁻¹ and half-life of 4-6 days (Singh *et al.*, 1990a).

Adsorption batch experiment: The sorption of Atrazine and Malathion on soil was studied using a batch experiment technique as described in EPA (1991) and Chefetz *et al.* (2004). Solutions with different initial Atrazine or Malathion concentrations (C_i) of 0, 15, 30, 45, 60, 90, 120, 240, 360, 480 and 600 µg L⁻¹ in 50 µM L⁻¹ CaCl₂ (as background solution for control the ionic strength of adsorbate solution) were used in duplicate. Adsorption was initiated by mixing 2.0 g of air-dried soil

Table 1: Some physical and chemical characteristics of soil used in present study

Parameter	Value	Unit
Particle size distribution		
Sand	81.9	%
Silt	2.5	%
Clay	15.6	%
Textural class	Sandy loam	
Calcium carbonate content	9.29	%
Organic matter content	0.05	%
pH (soil paste extract)	8.30	
Ec, (soil paste extract)	0.92	dS m ⁻¹
Soluble cations		
Ca ²⁺	6.25	meL ⁻¹
Mg ²⁺	2.00	meL ⁻¹
Na ⁺	1.60	meL ⁻¹
K ⁺	0.45	meL ⁻¹
Soluble anions		
CO ₃ ²⁻	0.00	meL ⁻¹
HCO ₃ ⁻	3.00	meL ⁻¹
Cl ⁻	2.00	meL ⁻¹
SO ₄ ²⁻	5.30	meL ⁻¹

sample with 25 mL of the various Atrazine or Malathion solutions in 50 mL centrifuge tube. The tubes were mechanically shaken for 8 h at 25±2°C and then equilibrated up to 24 h. The suspensions were centrifuged at 10000 rpm. The supernatant was used for analyzing the Atrazine and Malathion.

The sorbed pesticides (S) were calculated as the difference between the initial (C_i) concentration and equilibrium concentration (C_e) as follows (Eq. 1):

$$S = \frac{V_w \times (C_i - C_e)}{M_{soil}} \quad (1)$$

Where:

- S = The pesticide concentration on the solid phase at equilibrium (µg g⁻¹)
- V_w = The volume of pesticide solution (mL)
- C_i = The initial concentration of pesticide in solution (µg L⁻¹)
- C_e = The equilibrium concentration of pesticide in solution (µg L⁻¹)
- M_{soil} = The mass of solid phase (soil) (g)

Mathematical fitting of the adsorption isotherms: The sorption data were fitted in some mathematical models to obtain the sorption parameters of pesticides. The mathematical models are shown in Table 2, the sorption isotherm models are linear, Freundlich and Langmuir.

Pesticide degradation: The pesticides were dissolved in methanol solvent and allow to methanol volatilization in conical flask, then 200 g of soil sample were mixed at field capacity (Hyzak and Zimdahl, 1974). The mixture was mixed thoroughly for homogenous distribution of pesticides. After desired time of incubation (at room

temperature, 25±2°C), soil sample was taken at time intervals; 0, 1, 2, 4, 6, 8, 10, 15, 20 and 25 days for extraction and analysis of pesticide residues.

Pesticide dissipation half-life is defined the time required for pesticide concentration to be half of its initial value due to many processes such as degradation and volatilization. Pesticide dissipation is represented by the first-order rate equation:

$$\frac{dC}{dt} = -kt \quad (2)$$

where, dC/dt is the change in concentration C with respect to time t and k is first-order dissipation rate coefficient (degradation rate constant). By mathematical transformation, the previous equation becomes:

$$C = C_0 \times \exp(-kt) \quad (3)$$

where, C₀ is the initial concentration of pesticide (t = 0). When C = 0.5C₀, the pesticide half-life (t_{0.5}) is given by:

$$t_{0.5} = \frac{\ln(2)}{k} \quad (4)$$

Pesticide residues extraction and analysis: Pesticide residues in solution were extracted with acetone: hexane, using ratio of 3:2 (v/v) extraction solution using Microwave-Assisted Extraction Technique (MAE) as described by Westbom *et al.* (2008). The pesticide concentrations in the extract were analyzed by gas chromatography (Hewlett-Packard, Agilent 6890N), equipped with Nitrogen-Phosphorus Detector (NPD) and Electron Capture Detector (ECD) (Westbom *et al.*, 2008). The clear supernatant was used for analyzing the pesticides concentration (C_e) using gas chromatography, GC-MS (Agilent-6890, USA, using 30 m × 0.25 mm × 0.25 μm film cross-linked with 5% phenyl methyl silicone capillary column and a N/P detector). The operational conditions of the gas chromatography were: injector

temperature 250°C, detector temperature 320°C, initial oven temperature 80°C with a holding time of 2.5 min, increased to 230°C at 40°C min⁻¹ with a final holding time of 3 min and carrier flow rate 1.5 mL min⁻¹. All the solutes were rectified using external standard solution of Atrazine or Malathion. The detection limit was below 5 μg L⁻¹.

RESULTS AND DISCUSSION

The equilibrium distribution of the two pesticides in sorbed and solution phases were summarized in Table 3. Similarly the equilibrium solution concentration (μg L⁻¹) and sorbed phase concentration (μg g⁻¹) are presented in Table 3 against applied concentration of both pesticides. Both solution and sorbed phase were increased with the increasing of the amount of applied pesticides.

The most common types of sorption isotherms are the Freundlich (1906), Langmuir (1916) and although others are available such as Redlich and Peterson (1959), Toth (1995), Temkin isotherms (Temkin and Pyzhev, 1940). We must take in account that these models do not reflect any mechanisms of sorbate uptake; the equations are just capable of reflecting the experimental data. These isotherms view S (adsorbed pesticide) as a function of the C_e (equilibrium concentration), in accordance to the equilibrium distribution of pesticide molecules between aqueous and solid phases as the C rises. Equilibrium isotherms are usually measured to determine the capacity of the solid phase sorbent for solution ions.

Linear isotherm: Sorption of pesticides by soils is generally referred to partitioning effect of organic compounds between soluble and solid phases and can describe by linear isotherm (Wu and Gschwend, 1986). It could be seen that the sorption behavior of both Atrazine and Malathion fitted linear isotherm Eq. 5 in the

Table 2: The sorption isotherm models used in the present study

Isotherm	Formula and definition
Linear (Wu and Gschwend, 1986)	$S = K_d \times C_e$ (5) S = pesticide sorbed concentration (μg g ⁻¹) C _e = equilibrium concentration of pesticide in suspension (μg L ⁻¹) K _d = linear partition coefficient (L g ⁻¹)
Freundlich (Freundlich, 1906)	$S = K_f \times C_e^n$ (6) K _f = Freundlich isotherm coefficient (L g ⁻¹) n = degree of isotherm
Langmuir (Langmuir, 1916)	$S = \frac{S_m \times b \times C_e}{1 + b \times C_e}$ (7) S _m = maximum sorption capacity (μg g ⁻¹) b = Langmuir constant (L μg ⁻¹)

Table 3: Equilibrium distribution of the Atrazine and Malathion pesticides between solution and solid phases

Pesticide applied (μg L ⁻¹)	Atrazine herbicide		Malathion insecticide	
	Equilibrium solution (μg L ⁻¹)	Sorbed phase (μg g ⁻¹)	Equilibrium solution (μg L ⁻¹)	Sorbed phase (μg g ⁻¹)
0	0.000	0.000	0.000	0.000
15	0.050	0.187	0.150	0.186
30	0.100	0.374	0.320	0.371
45	0.140	0.561	0.470	0.557
60	0.210	0.747	0.630	0.742
90	0.330	1.121	0.950	1.113
120	0.410	1.495	1.280	1.484
240	0.720	2.991	2.550	2.968
360	1.100	4.486	3.730	4.453
480	1.730	5.978	5.100	5.936
600	3.000	7.463	7.000	7.388

Table 4: Sorption fitting parameters of Atrazine and Malathion pesticides

Isotherm type	Parameters	Atrazine			Malathion		
		Estimate	R ²	SSE	Estimate	R ²	SSE
Linear	K _d	3.2997	0.9765	1.8305	1.1162	0.9956	0.3279
Freundlich	K _f	3.6420	0.9885	0.7982	1.2591	0.9975	0.1795
	n	0.8334			0.9263		
Langmuir	S _m	22.2197	0.9948	0.3611	46.2552	0.9987	0.0956
	b	0.2084			0.0284		

concentration range 0 to 600 µg L⁻¹. The linear partition coefficient (K_d) and determination coefficient (R²) for the fit of the data to Eq. 2 were shown in Table 4. The partition coefficient (K_d) values varied between the two pesticides. The K_d value of Atrazine was 3.2997 L g⁻¹, it is higher than that of Malathion (K_d=1.1162 L g⁻¹) (Table 4).

Results showed that there are a significant relationship between partition coefficient and solubility of organic compounds (Chiou *et al.*, 1977; Chiou, 1981). It means that if solubility of pesticide is small, then the partition coefficient will be high. The present results confirms this fact, where Atrazine has low solubility value (S_w = 30 mg L⁻¹) and high partition coefficient (K_d = 3.2997 L g⁻¹), while Malathion has high solubility value (S_w = 145 mg L⁻¹) and low partition coefficient (K_d = 1.1162 L g⁻¹). Based on sorption results, one may regard Atrazine and Malathion sorption by soil as essentially linear for most reaction times. The lack of nonlinear or concentration-dependent behavior of sorption pattern is indicative of lack of heterogeneity of sorption-site energies. The K_d parameter is more meaningful for comparison between pesticides, soils and reaction times. Therefore, Atrazine herbicide has more retention ability on soil than Malathion and this was confirmed by the partition coefficient values. Accordingly, the Malathion has more ability to runoff or downward movement in soil, than Atrazine that has less ability to movement in soil and concentrated in the soil surface layer. The strong Atrazine retention by the soil as indicated that K_d value (Table 4) is highly beneficial in minimizing potential runoff and downward movement in the soil and into the groundwater (Selim, 2003; Selim *et al.*, 2003; Abdel-Nasser, 2006).

Freundlich isotherm: Sorption parameters (K_f and n) of Atrazine and Malathion in soil are presented in Table 4. The K_f parameter represents the empirical constant of the Freundlich isotherm, Eq. 6 (Freundlich, 1906) and expressing soil sorbent capacity for a given range of pesticide concentration such as partition coefficient (K_d). In our study, the K_f values were 3.6420 and 1.2591 L g⁻¹ for Atrazine and Malathion, respectively (Table 4). K_f value were found to be correlated with some soil properties such as pH and/or organic matter content and

can be varied according soil type (Weber *et al.*, 2004). The high value of K_f (such as Atrazine) could be related to strong affinity to the solid phase (Laabs *et al.*, 2000). In contrast, the low value of K_f such as Malathion could be related to the high affinity to the liquid phase (Clausen and Fabricius, 2001).

Concerning the Freundlich parameter (n) values, the present results are 0.8334 and 0.9263, respectively for Atrazine and Malathion. It is inferior to 1.0 (Table 4). The slopes (n) of Freundlich isotherms is the measure of the intensity of sorption and reflects the degree to which sorption is the function of contaminant concentration, i.e., indicates that the initial concentrations of pesticides increased, the percentage adsorbed by the soil decreased. This correlation was more pronounced in case of Atrazine and Malathion. This might be explained by an increased difficulty to access the adsorption sites when pesticide concentrations are elevated. The n values for Atrazine and Malathion were near unity suggesting C-type of adsorption isotherm (Giles *et al.*, 1960). This type of adsorption isotherms is observed when the molecules are sorbed in a flat position, not suffering a strong competition, which explain the high affinity to sorbent for solute at low concentrations. However, as the concentration increases sorption sites become limiting, therefore, sorption decreases. Konstantinou and Albanis (2000) and Majumdar and Singh (2007) have reported L-type adsorption isotherms for pesticide sorption in fly ash-soil mixtures. The values of determination coefficient (R²) for all the cases were very high (R²>0.98), indicating that the Freundlich adsorption isotherm equation satisfactorily explained the results of herbicide sorption in soil and the results were significant at 99% levels.

Langmuir isotherm: Sorption parameters (S_m and b) of Atrazine and Malathion on soil are presented in Table 4. The S_m parameter represents the maximum adsorption capacity of the Langmuir isotherm, Eq. 7 (Langmuire, 1916). In the present study, the S_m values were 22.22 and 45.44 µg g⁻¹ for Atrazine and Malathion, respectively. The S_m value can be correlated with some soil properties such as clay and organic matter content and can be varied according soil type.

Concerning the Langmuir parameter (*b*) values, the present results were 0.2084 and 0.0284 L μg⁻¹, respectively. There are represent the adsorption energy of Atrazine and Malathion pesticides. The constant *b* of Langmuir isotherm is the measure of the affinity of the solid phase to adsorb the pesticide molecule and reflects the degree to which sorption is the function of solid material. As the *b* constant increased, the binding power of pesticide molecule to solid phase increased. The present results indicate that Atrazine has higher affinity of binding to soil particles than Malathion. In other words, Atrazine has relatively high affinity for solid phase, while Malathion has higher affinity for solution phase.

The effect of isotherm shape can be used to predict whether a sorption system is 'favorable' or 'unfavorable'. The essential feature of the Langmuir isotherm can be expressed mathematically by dimensionless constant separation factor or equilibrium parameter *K_R*, which is defined by the following relationship (Zhai *et al.*, 2004):

$$K_R = \frac{1}{1 + b \times C_0} \quad (8)$$

where, *C₀* is the initial concentration (μg L⁻¹). The parameter *K_R* indicates the shape of the isotherm accordingly:

Value of <i>K_R</i>	Type of isotherm
<i>K_R</i> > 1	Unfavorable
<i>K_R</i> = 1	Linear
0 < <i>K_R</i> < 1	Favorable
<i>K_R</i> = 0	Irreversible

The values of *K_R* for Atrazine and Malathion indicate that sorption is more favorable for the range of concentration used. The sorption is very favorable for Malathion than Atrazine.

Proposed isotherm: Sorption process of Atrazine and Malathion on soil is proposed using the Exponential form as follows:

$$S = S_m \times (1 - \exp(-K_a \times C_e)) \quad (9)$$

where, *K_a* is the sorption equilibrium constant (L μg⁻¹).

Sorption parameters (*S_m* and *k_a*) of Atrazine and Malathion on soil are presented in Table 5. The Exponential sorption isotherm of Atrazine and Malathion is illustrated in Fig. 1a and b.

The *S_m* parameter represents the maximum adsorption capacity of the Exponential isotherm, Eq. 9 (proposed isotherm). For the proposed model, the *S_m* values were 12.85 and 24.57 μg g⁻¹ for Atrazine and Malathion, respectively (Table 5). The *S_m* value can be correlated with some soil properties such as clay and organic matter content and can be varied according soil type.

Concerning the *k_a* values, the obtained results were 0.3564 and 0.0523 L μg⁻¹ for Atrazine and Malathion, respectively (Table 5). It represents the adsorption energy of Atrazine and Malathion pesticides on soil. The constant *k_a* of Exponential isotherm is the measure of the affinity of the solid phase to adsorb the pesticide molecules and reflects the degree to which sorption is the function of pesticide concentration. As the *k_a* constant increased, the binding power of pesticide molecule to solid phase increased. The present results indicate that Atrazine has higher affinity for binding to soil particles than Malathion. The present result states that Atrazine will reach the maximum adsorption at 28 μg L⁻¹ Atrazine concentration in solution, while Malathion does not reach the maximum capacity at this concentration.

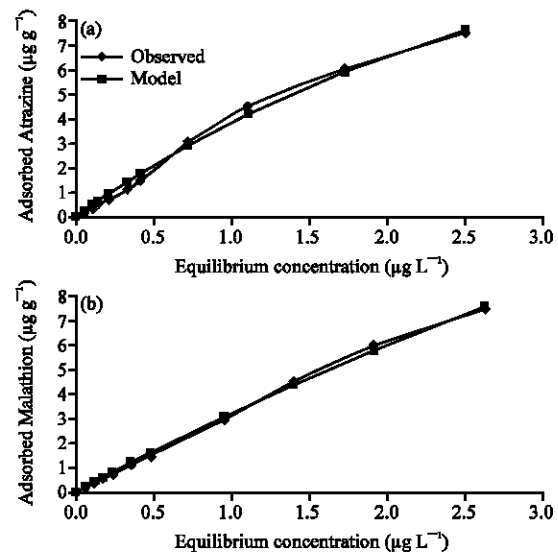


Fig. 1: Exponential sorption isotherm for (a) Atrazine and (b) Malathion on soil

Table 5: Sorption fitting parameters of Atrazine and Malathion pesticides for the proposed model

Isotherm type	Parameters	Atrazine			Malathion		
		Estimate	R ²	SSE	Estimate	R ²	SSE
Exponential (proposed model)	<i>S_m</i>	12.8497	0.9953	0.33249	24.5720	0.9987	0.0913
	<i>K_a</i>	0.3564			0.0523		

The present results indicate that the three isotherms; Freundlich, Langmuir and Exponential have similar accuracy in predicting the sorption process of Atrazine and Malathion in which they have similar R^2 values, but the proposed (Exponential) isotherm is better because it has high R^2 and less SSE.

Degradation rate and Half-life calculations: Figure 2a and b show the variation in Atrazine and Malathion mass in the soil during the degradation period. A highly atrazine concentration was observed than Malathion. Measured degradation rate averaged about 0.0102 day^{-1} for Atrazine, while the degradation rate of Malathion was 0.1053 day^{-1} . The half-lives were accounted as 68.1 and 6.6 days for Atrazine and Malathion, respectively. These values are close up of the values reported in many references, Ghadiri *et al.* (1984), Singh *et al.* (1990b) and Vargha *et al.* (2005). The present results indicated that Malathion was more degradable than Atrazine. Therefore, Atrazine is more stable in soil than Malathion. About 78% of Atrazine was remained in soil at 25 days after application, while 8% only of Malathion was remained in soil at the same period.

Several reasons can justify the decrease in pesticides concentration in the soil i.e., volatilization, Photo-, chemical and biological degradation. These processes may be the most important mechanism for pesticides dissipation (Ostrowsky *et al.*, 1997; Tasli *et al.*, 1996). Low organic carbon and clay content reduce the soil capacity to absorb pesticides, therefore it will be more available to leaching (Fermanich *et al.*, 1996). Results also indicated that atrazine does not have high mobility than Malathion; resulted in the highest atrazine concentration was always

found in the surface soil layer (Rocha, 1989; Ying and Williams, 2000; Abdel-Nasser, 2001, 2006).

Sorption equilibrium has important environmental process that determines the fate, transport and toxicological impact of pollutants in ecosystem to reach the groundwater. In addition to affecting the mobility of pollutants and directly influence the pathways and transformation rates of pollutants by associated chemical and microbial processes. Because sorption and degradation are the two most important processes governing fate and transport of chemical contaminants in the environment, a comprehensive understanding of their relationship would help in the management of pesticides in agricultural fields and in the assessment of their potential to contaminate groundwater.

CONCLUSIONS

The findings from this study emphasize on the need for care when using persistent pesticides to control weeds in soil. To reduce possible residues in soil and crop damage, it is better to select short-residual pesticides and use the lowest available application rate to soil. It is also important to apply pesticides during optimum weather conditions in order to avoid spray drift of pesticides and movement of the pesticides caused by heavy rains following the application into the groundwater.

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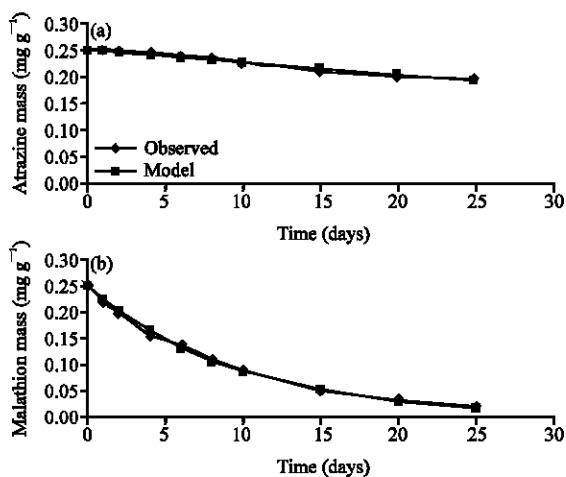


Fig. 2: (a) Atrazine and (b) Malathion degradation curves in soil

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