

ATRAZINE ADSORPTION DESORPTION BEHAVIOR IN DAREHASALUIE KAVAR CORN FIELD SOIL IN FARS PROVINCE OF IRAN

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ABSTRACT

Adsorption-desorption behaviors of widely applied atrazine soil were studied, employing a batch technique as a case study in Darehasaluie Kavar corn field in Fars Province in 2005. Samples were collected from 0 to 20 cm soil depth, where was cultivated under a crop rotation (corn-wheat) during the past 10 years. Sorption kinetics exhibited two phenomena: an immediate rapid sorption (1.31 µg/g soil after 12 h) followed by a slow sorption process (1.37 µg/g soil after 24 h). Desorption behavior of atrazine was similar to its adsorption, but at a very slower rate. Atrazine desorption efficiencies were much less effective and incomplete even after a long equilibration time (only 9.16% after 96 h). The adsorption-desorption rate for most of the time was positively related to the amount of applied atrazine and the time required for equilibration ($P < 0.01$). Desorption data exhibited hysteresis phenomena. Atrazine adsorption data described well according to Freundlich ($r^2 = 0.95$), Langmuir ($r^2 = 0.82$) and Temkin ($r^2 = 0.84$) isotherms. However, the fit to Freundlich adsorption model in a non-linear form ($1/n < 1$) was closer than the others. Desorption isotherm could be well described by the Temkin ($r^2 = 0.96$) and Freundlich ($r^2 = 0.92$) isotherms, but the fit to Temkin model was closer than that of Freundlich.

Key words: Adsorption, desorption, atrazine, isotherm, hysteresis phenomena

INTRODUCTION

Atrazine (2-chloro-4-ethyl amino-6-isopropyl amino-1, 3, 5-triazine), the most widely used herbicide, has been used as pre-and-post-emergent herbicide to control broad-leaf weed in the production of corn (Jones *et al.*, 1982). Atrazine is frequently detected in groundwater and surface water resources (Putnam, 1997; Miler *et al.*, 2000). Atrazine is moderately persistent in the environment with the half-life of one to twelve months. However, the herbicide has been reported to persist in soils for up to a decade (Caprieli *et al.*, 1985).

Atrazine has recently been reported to have long-term reproductive and endocrine-disrupting effects (Colborn *et al.*, 1993). Atrazine is a probable human carcinogen (Van Leewen *et al.*, 1999).

International Agency for Research on Cancer (IARC), 1991 has concluded that there is

inadequate evidence in human and limited evidence in experimental animals for the carcinogenicity of atrazine (Group 2B). The maximum contaminant level (MCL) for atrazine in drinking water established by the USEPA is 3.0 µg/L and the European Union requires the MCL below 0.1 µg/L for a single pesticide in drinking water.

The fate of atrazine in soil depends upon several factors including sorption to soil component, uptake by plants, transport via runoff and leaching, biodegradation, photodegradation, volatilization, and chemical degradation. Adsorption-desorption of atrazine to soil components are key processes that can control several other factors. For example, the herbicide is being shielded from biodegradation, possibly through sorption to natural organic matter. Adsorption directly influences various processes, such as leaching and degradation (Koskinen, 1990). Adsorption of atrazine to various soil components has been widely studied (Chung

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et al., 2002 and Dorado *et al.*, 2003). Cellis and his coworkers (1997) showed that atrazine sorption to natural organic matter was higher than that to clay mineral. However, others indicated that atrazine adsorption to clay mineral was significant (Roy and Krapac, 1994). Desorption is a critical process affecting the extent of release of pesticides from the soil. Many studies have reported irreversible sorption and the occurrence of hysteresis phenomena; therefore, less herbicide was desorbed than predicted by adsorption isotherms (Brusseau and Rao, 1989; Moreu, and Mouvet, 1997; Huang *et al.*, 1998; Gao *et al.*, 1998 and Altfelder *et al.*, 2000). The degree of irreversibility of the adsorption plays a significant role in determining the mobility of pesticide in soil. Therefore, it is directly related to herbicide runoff and leaching that leads to surface and groundwater contamination, respectively. Understanding sorption kinetics allows prediction of how fast such a reaction reaches equilibrium and the possible mechanisms involved. For herbicides, in particular atrazine, kinetic studies may provide important information related to atrazine fate in soil. Adsorption isotherms, such as Freundlich, Langmuir and Temkin, are often used to describe the overall sorption characteristics of a particular soil at equilibrium with a range of contaminant concentrations. During the last few years, Fars province (in southern Iran) has been the first in wheat and corn production in the country. Atrazine has widely been used to control broad leaf and grassy weeds in agricultural corn fields. Therefore, the objectives of the research were to (i) study the adsorption-desorption behavior of atrazine and (ii) evaluate atrazine distribution on the soil using sorption parameters. The impact of sorption hysteresis was also studied, developing a specific understanding of atrazine associations with the soil in Darehasaluie Kavar Corn Field (DAKCF) in Fars Province in 2005 and the feasibility to pollute the groundwater.

MATERIALS AND METHODS

Reagents

All chemicals were purchased from Merck (Germany). Atrazine standard was supplied by

Acqua Standard Europe, Switzerland.

Soil sampling and processing

Soil samples into 0 to 20 cm soil depth from the Darehasaluie Kavar Corn Field (DAKCF) under corn cultivation were collected with a hand-driven soil auger in September 2004. The soil samples were air-dried in dark in room temperature and screened through a 2.0 mm sieve for maintaining homogeneity of soil in order to reduce the variability of adsorption data (Sonon and Schwab, 1995). 30 mL of dichloromethane was added to 10 g of the soil sample and shaken in a reciprocal shaker for 20 minutes. After filtration, the organic phase was transferred to a separating funnel and then atrazine was extracted with 20 mL HCl (0.01N). Square wave voltammetry with the Hanging Mercury Drop Electrode (Auto Lab type analyzer equipped with Metrohm VA STAND 663 and GPES 4.9 software) was used in this study to determine atrazine residual concentration in soil samples (Luciana *et al.*, 2004). Atrazine recovery percent from soil with this method of extraction was 98%. Hydrometer was used to determine the soil texture. Other soil characteristics such as soil solution pH (Thomas, 1996), organic matter content (OM) (Darrel and Nelson, 1996), and cation exchange capacity (CEC) (Summer and miller, 1996) were determined. The general physico-chemical characteristics were as follows: soil texture; loam; clay 17.06%, silt 31.5%, sand 47.14%; pH=7.94; OMC=8.8 gkg⁻¹ soil; CEC=11.12 mole (+) kg⁻¹ soil.

Adsorption-desorption experiments

The adsorption-desorption experiments were carried out in duplicates in the batch mode according to guideline 106 (Anonymous, 1981), which was modified in this study. The operational conditions were: pH=7; temperature=23°C; soil: solution ratio=1:5; absence of light; addition of two drops of toluene to each tube to inhibit microbial growth; shaking time=24 h.

A series of 25 mL of 0.01 M CaCl₂ solutions containing 0.406, 0.812, 1.489 and 5.144 μg/L atrazine, respectively, was added to 5 g of soil in glass centrifuge tube and shaken in a horizontal agitator (Galnhamp, England) for 2, 12, 18, and 24 hours, respectively. 0.01 M CaCl₂ was added to adjust the ionic strength of the solutions at approximately the same level and to provide a

constant background electrolyte. Then the suspensions were centrifuged at 4800 rpm for 30 minutes. Blank and control samples were prepared in the same manner without atrazine or soil. Average system losses were less than 6% of initial solute concentration. Amounts of the adsorbed pesticides were calculated as the difference between the initial atrazine concentration and the supernatant concentration at equilibrium.

Desorption studies were carried out for atrazine with four different concentrations. After the adsorption process, the supernatant was replaced by a similar volume of 0.01 M CaCl₂ solution, with no atrazine. The suspensions were shaken as in the adsorption studies. The desorption equilibrium process was done for (2, 12, 24, 48, 72 and 96 hours) four times for each tube. The atrazine concentration in the solution was determined after each desorption step. The amount of atrazine remaining adsorbed on the soil was calculated as the difference between the initial adsorbed and desorbed amounts.

After determining atrazine concentration in liquid and solid phase at different equilibration periods, the equilibrium concentration (C_e) is measured. Three adsorption isotherms (Freundlich, Langmuir and Temkin) are examined for atrazine adsorption-desorption data on DAKCF soil. According to the atrazine adsorption data, the fit of Freundlich, Langmuir and Temkin isotherms have been determined by drawing the logarithmic equilibrium concentration in the liquid and solid phase. Adsorption isotherm parameters were calculated for atrazine using the Freundlich equation:

$$\log \frac{x}{m} = \log K_f + \frac{1}{n} \log C_e \quad (1)$$

Where:

x/m (mg/kg) is the amount of atrazine adsorbed per kg of soil. C_e (mg/L) is the equilibrium concentration in solution; K_f (L/kg) and $1/n$ are the adsorption coefficients and the adsorption constant, respectively. The Langmuir equation (2) and the Temkin equation (3) were also used to fit the adsorption data:

$$\frac{C_e}{C_s} = \left[\frac{1}{(Kb)} \right] + \left(\frac{1}{b} \right) C_e \quad (2)$$

$$C_s = K_1 + K_2 \ln C_e \quad (3)$$

Where:

K and b are adsorption coefficients. K_1 and K_2 are sorption constants, and C_s and C_e are as defined above.

Desorption was also described by the same equations. Statistical analysis was performed by linear regression to calculate the isotherm coefficients K_f and $1/n$. The means of three replications were used for calculation of the isotherms. The repeated measurement design was used to calculate least significant differences of adsorption and desorption concentration of atrazine over the equilibration time.

RESULTS

Atrazine adsorption desorption

After the equilibration periods, atrazine adsorption concentrations at 4 different concentrations were measured and shown in Tables 1. The adsorption efficiency of atrazine exhibited an immediate rapid sorption by which about 41-75% of the added atrazine adsorbed within 12 h depending on initial atrazine concentration, followed by a slow sorption over a longer period. As shown in Figure 1, atrazine concentration increased as the adsorption time increased. Atrazine adsorption concentration increased as the applied atrazine concentration increased as well. After that, its rate became slow and then constant at 18 h of equilibration time. According to the results of statistical analysis for atrazine adsorption at different atrazine concentrations and equilibration time periods, it can be assumed that there is a relationship between atrazine adsorption concentration and all equilibration time periods ($P < 0.01$), except for the time period of 12 and 24 hrs ($P > 0.05$).

After adsorption studies, desorption behavior of atrazine in soil was studied. Atrazine desorption data were shown in Tables 2. The equilibrium time required for desorption (96 h) is much more than adsorption (24 h). After the first desorption step (24 h) only 4.98 to 35.5% of the total adsorbed amount of atrazine was desorbed, depending on the initial atrazine concentration. The percent of atrazine desorption increased as the equilibration periods increased. Atrazine desorption after 96

hours of equilibration time were between 9.16 and 54.11%. As it shown in Fig. 2, atrazine desorption efficiency decreased as the equilibration time increased and then became constant. According to the results of statistical analysis for atrazine desorption at different atrazine concentrations and equilibration time periods, it can be concluded that there is a relationship between atrazine desorption concentration and all equilibration time periods ($P < 0.01$), except for the time period of 12 and 48 hrs and also for 72 and 96 hrs ($P > 0.05$).

Adsorption desorption isotherms

The conformity of adsorption data for the DACFS soil to Freundlich, Langmuir and Temkin isotherms (Fig. 3 to Fig. 5) are indicated by the coefficient of determination (r^2). The atrazine adsorption data described well to Freundlich, Langmuir and Temkin isotherms, respectively. However, the fit to Freundlich adsorption model ($r^2=0.95$) was greater than that of Langmuir ($r^2=0.82$) or Temkin ($r^2=0.84$). On the basis of the measured r^2 value, the atrazine adsorption conformity to different isotherms can be arranged in the following order: Freundlich adsorption > Temkin adsorption > Langmuir adsorption.

The atrazine desorption conformity to the isotherms can be arranged in the following order:

Temkin desorption > Freundlich desorption > Langmuir desorption

The fit to Temkin desorption model ($r^2=0.962$) is closer than that of Freundlich ($r^2=0.916$) but Langmuir desorption model does not fit adequately ($r^2=0.197$).

Table 1: Atrazine adsorption concentration at 4 different initial concentrations

Time (h)	Adsorption concentration* ($\mu\text{g/g}$ soil)			
	**a	b	c	D
2	0.48	0.61	4.25	5.9
12	1.31	2.09	5.6	10.75
18	1.36	2.16	5.95	11.4
24	1.37	2.29	6.0	11.7

* mean of three replications

** (a=0.406 mg/kg soil, b=0.812 mg/kg soil, c=1.489 mg/kg soil and d=5.144 mg/kg soil) in Darehasaluie Kavar corn field

Table 2: Atrazine desorption efficiency at 4 different initial concentrations

Time (h)	Desorption efficiency* (%)			
	**a	b	c	D
2	0.0	0.0	0.0	14.28
12	0.0	0.0	12.55	29.0
24	4.98	15	19.25	35.50
48	6.23	20	22.59	47.62
72	8.43	25	26.78	51.95
96	9.16	27	29.29	54.11

* mean of three replications

** (a=0.406 mg/kg soil, b=0.812 mg/kg soil, c=1.489 mg/kg soil and d=5.144 mg/kg soil) in Darehasaluie Kavar corn field

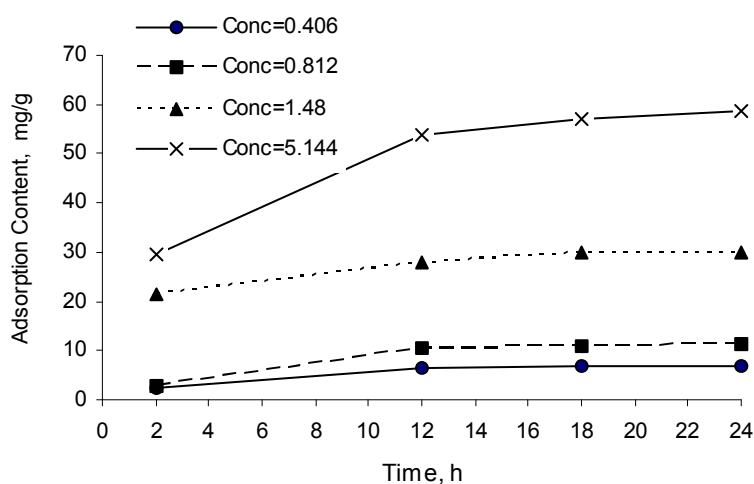


Fig. 1: Atrazine adsorption concentration in Darehasaluie Kavar corn field soil at different initial concentrations

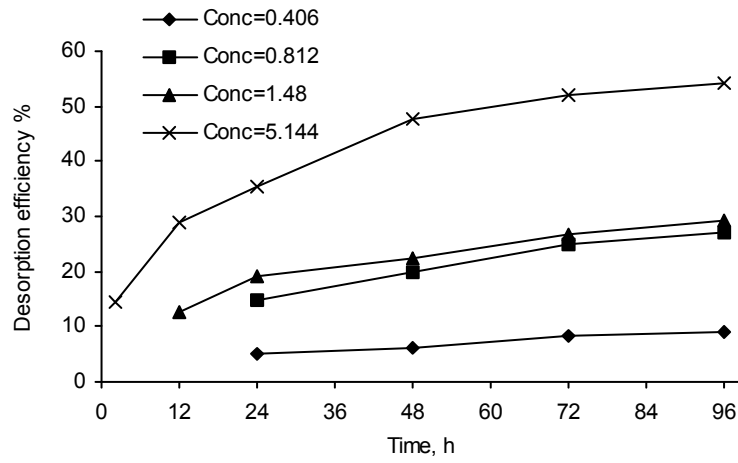


Fig. 2: Atrazine desorption efficiency in Darehasaluie Kavar corn field soil at different concentrations

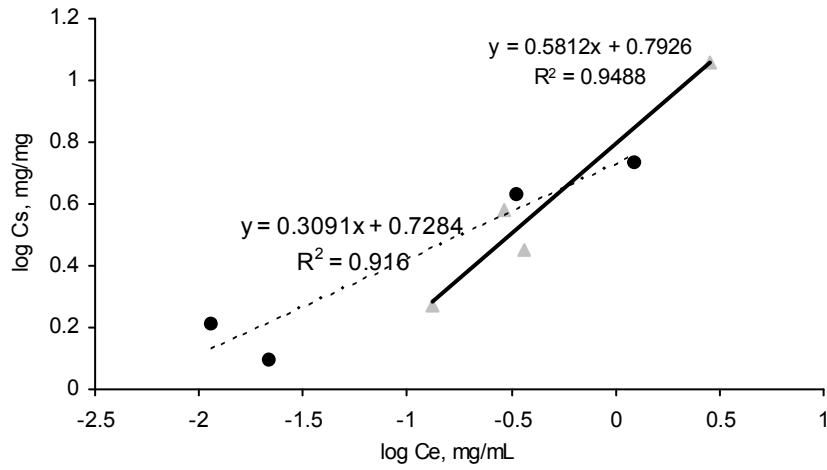


Fig.3: Freundlich adsorption-desorption isotherm for atrazine in Darehasaluie Kavar corn field soil

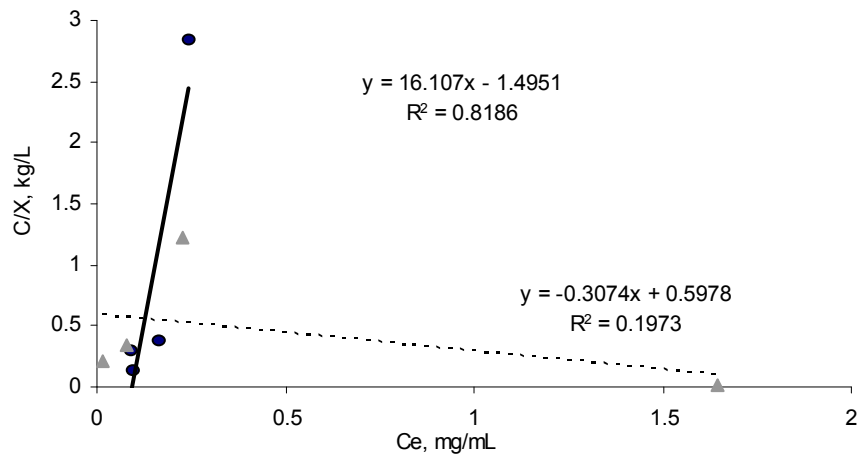


Fig. 4: Langmuir adsorption-desorption isotherm for atrazine in Darehasaluie Kavar corn field soil

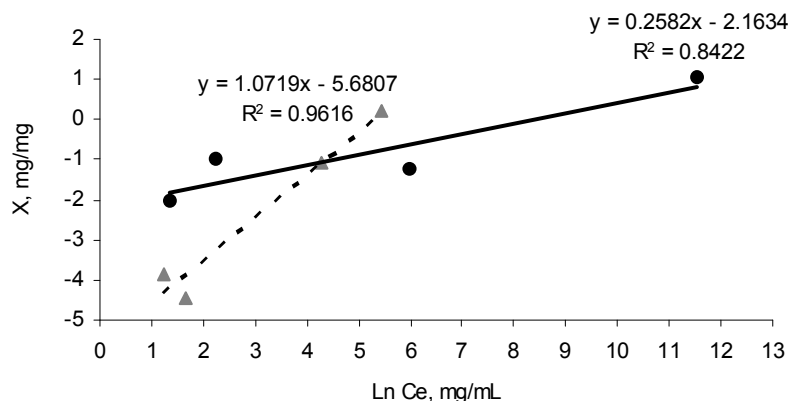


Fig. 5: Temkin adsorption-desorption isotherm for atrazine in Darehasaluie Kavar corn field soil

DISCUSSION

According to the results the adsorption concentration of atrazine increases as the adsorption time increases. After that, its rate becomes slow and then constant. Also, the adsorption concentration of atrazine increase as the applied atrazine concentration increases as well. Gao and his coworkers (1998) also found that the adsorption kinetics of many pesticides, including atrazine in sediments, had an initial steep slope reaching a plateau with a relative slow equilibration. Presumably initial quick adsorption is a surface phenomenon, followed by a slow migration and diffusion of the compound into the organic matter and soil mineral texture. Therefore, adsorption studies are very important and make it possible to evaluate retention of atrazine by soil colloids. In addition, understanding sorption kinetics allows prediction of how fast such a reaction reaches equilibrium and the possible mechanisms involved. For herbicides, in particular atrazine, kinetic studies may provide important information about atrazine fate in soil. The same phenomena occurred for atrazine desorption but at a very slower rate (Table 2). Therefore, even after the sixth desorption step, the adsorbed atrazine was not completely desorbed. This retarded desorption effect in soil may last days or even weeks. In addition, desorption curves show a flatter shape than adsorption curves. The higher rate of atrazine

desorption was observed as the applied atrazine concentrations increased. In other words, lower rate of non-desorbed atrazine was observed as the applied atrazine concentrations increased.

Over a limited range of atrazine concentration, nonlinear adsorption isotherm for Freundlich is observed for atrazine, which is poorly soluble and shows a relatively high K_{ow} value. Many researches have found that atrazine adsorption conformed to Freundlich isotherm and nonlinearity was also observed (Mersie *et al.*, 1999 and Nemeth-Konda *et al.*, 2002). The nonlinearity of surface adsorption phenomena may be attributed to adsorption into organic and mineral matrices (Brusseau and Rao, 1989). According to Freundlich isotherm, the fit to Freundlich isotherm to atrazine adsorption has been reported (Gao *et al.*, 1998 and Heater *et al.*, 2003). The adsorption coefficient (K_f), the adsorption constant $1/n_{ads}$ and desorption constant $1/n_{des}$ for Freundlich adsorption isotherm for atrazine are 4.56 (L/kg), 0.92 and 0.31, respectively. Desorption data exhibited hysteresis phenomena $[(1/n_{ads})/(1/n_{des})]=1.88$. This is illustrated by the different slopes $1/n$ of the adsorption and desorption isotherms. The compound with a value of $(1/n_{ads})/(1/n_{des})$ more than one exhibit a hysteresis. The mechanism of hysteresis is not clear yet, but the binding of compound to organic matter and mineral particles

is thought to be the most responsible factor (Brusseau and Rao, 1989). Several studies have illustrated hysteretic behavior of atrazine and its metabolites. The degree of hysteresis varied with soil type and soil organic matter. Hysteretic behavior of solutes in soils appears to occur when desorption based phase distribution is different from the one observed during sorption (Altfelder, *et al.*, 2000). In conclusion, the results reported in the sorption of atrazine in the soil of DAKCF revealed that atrazine added to soil was effectively and rapidly retained by its solid phase. The rate of atrazine adsorption showed an initial increase, reaching a plateau with a relative slow rate. The adsorption and desorption of atrazine increased with increasing applied atrazine to soil. Desorption behavior of atrazine was similar to its adsorption, but at a very slower rate. Therefore, atrazine adsorption in DAKCF soils was relatively high, but desorption was less effective and incomplete. Although, atrazine adsorption data showed a highly significant fit to Freundlich, Langmuir, and Temkin isotherms, the fit to Freundlich isotherm proved to be more suitable, as compared with Langmuir and or Temkin. However, the fit to Temkin desorption model was closer than that of Freundlich.

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